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Fourth Symposium on Chemical Evolution and the Origin and Evolution of Life

Proceedings of a symposium held at
NASA Ames Research Center
Moffett Field, California
July 24–27, 1990

NASA

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Fourth Symposium on Chemical Evolution and the Origin and Evolution of Life

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FOURTH SYMPOSIUM ON CHEMICAL EVOLUTION AND THE ORIGIN AND EVOLUTION OF LIFE

July 24-27, 1990
NASA Ames Research Center, Moffett Field, CA

Sponsored by
National Aeronautics and Space Administration
Life Sciences Division

Symposium Organizer: Robert A. Wharton
NASA Headquarters
Washington, D. C.

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Preface

This report contains session summaries and abstracts from the ***Fourth Symposium on Chemical Evolution and the Origin and Evolution of Life***, organized on behalf of NASA's Exobiology Program and held July 24-27, 1990 at NASA's Ames Research Center, Moffett Field, California.

The Symposium provided an opportunity for NASA Exobiology principal investigators to present their most recent research in a scientific meeting forum. In addition, the symposium helped foster increased communication across disciplinary lines, formulate a more integrated program approach, review progress in all tasks, and increase visibility of the Exobiology Program. The goal of NASA's Exobiology Program is to understand the origin, evolution, and distribution of life in the universe. The Exobiology Program is therefore quite broad in scope and subject areas covered during the Symposium included: Cosmic Evolution of the Biogenic Compounds, Prebiotic Evolution, Early Evolution of Life, Evolution of Advanced Life, Solar System Exploration, and the Search for Extraterrestrial Intelligence.

The more than 200 participants included Exobiology grantees, NASA Ames Research Center staff, graduate students and invited guests. Current plans are to continue to schedule this symposium every three years .

Further information about NASA's Exobiology Program can be found in the annual "Life Sciences Accomplishments Document," obtainable from the NASA Headquarters Life Sciences Division.

Robert A. Wharton, Jr.
Life Sciences Division
NASA Headquarters

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Fourth Symposium on Chemical Evolution and the Origin and Evolution of Life
July 24-27, 1990
NASA Ames Research Center, Moffett Field, California
N201, Main Auditorium

Session Schedule

Speakers are indicated with an asterisk.

Tuesday, July 24, 1990

9:00 AM Welcome

Dave Morrison and Dale Compton

9:10 AM Announcements

Robert Wharton

9:15 AM State of Exobiology

John D. Rummel

Session I: Cosmic Evolution of Biogenic Compounds

Chairman: Ted E. Bunch

9:40 AM "The Chemistry of Dense Interstellar Clouds"

W.M. Irvine*

10:00 AM "Theoretical Studies of the Extraterrestrial Chemistry of Biogenic Elements and Compounds"

D.J. DeFrees*

10:20 AM **Coffee Break**

10:40 AM "Measurement of the Spectral Signature of Small Carbon Clusters at Near and Far Infrared Wavelengths"

J.Tarter* and R. Saykally

11:00 AM "Laboratory and Observational Study of the Interrelation of the Carbonaceous Component of Interstellar Dust and Solar System Materials"

L.J. Allamandola*, S.A. Sanford, W.A. Schutte and A.G.G.M. Tielens

11:20 AM "Quantification of UV Simulated Ice Chemistry: CO and CO_2"

V.G. Anicich*, T. Arakelian and M.S. Hanner

11:40 AM "Volatiles in Interplanetary Dust Particles and Aerogels"

E.K. Gibson, Jr.* and C.P. Harmetz

12:00 noon "Isotopic Composition of Murchison Organic Compounds: Intramolecular Carbon Isotope Fractionation of Acetic Acid. Simulation Studies of Cosmochemical Organic Synthesis"

G.U. Yuen*, J.R. Cronin, N.E. Blair, D.J. Des Marais and S. Chang

12:20 PM **Lunch**

Session II: Solar System Exploration I

Chairman: Rocco L. Mancinelli

2:00 PM "Intact Capture of Cosmic Dust"

P. Tsou*

2:20 PM "Exobiological Implications of Dust Aggregation in Planetary Atmospheres: An Experiment for the Gas-Grain Simulation Facility"

J.L. Huntington*, J.R. Marshall and D.F. Schwartz

2:40 PM "Stable Carbon Isotope Measurements Using Laser Spectroscopy"

T.B. Sauke* and J.F. Becker

3:00 PM **Coffee Break**

3:20 PM "Paleolakes and Life on Early Mars"

M.A. Meyer, R.A. Wharton, Jr.* and C.P. McKay

3:40 PM "Subsurface Microbial Habitats on Mars"

P.J. Boston* and C.P. McKay

4:00 PM "Paleobiomarkers and Defining Exobiology Experiments for Future Mars Experiments"

R.L. Mancinelli*, L.J. Rothschild and M.R. White

4:20 PM "Conceptual Designs for In Situ Analysis of Mars Soil"

C.P. McKay, A.P. Zent* and H. Hartman

4:40 PM "Spectroscopy and Reactivity of Mineral Analogs of the Martian Soil"

A. Banin, J. Orenberg* and T. Roush

5:00 PM "Midinfrared Spectral Investigations of Carbonates: Analysis of Remotely Sensed Data"

T. Roush*, J.B. Pollack and C.P. McKay

5:20 PM **Adjourn**

8:00 PM **Special Session: The Space Exploration Initiative**

Matthew Golombek and John D. Rummel

Wednesday, July 25, 1990

Session III: Prebiotic Evolution

Co-Chairmen: Sherwood Chang/ Robert MacElroy

8:30 AM "Isotopic Constraints on the Origin of Meteoritic Organic Matter"

J.F. Kerridge*

8:50 AM "Kinetic Conversion of CO to CH_4 in the Solar System"

Y.L. Yung*, M. Allen and J.P. Pinto

9:10 AM "Production of Organic Compounds in Plasmas: A Comparison Among Electric Sparks, Laser-Induced Plasmas and UV Light"

T.W. Scattergood*, C.P. McKay, W.J. Borucki, L.P. Giver, H. Van Ghyseghem, J.E. Parris and S.L. Miller

9:30 AM "Organic Synthesis in the Outer Solar System: Recent Laboratory Simulations for Titan, the Jovian Planets, Triton and Comets"

C. Sagan*, W.R. Thompson, B.N. Khare and C.F. Chyba

9:50 AM **Coffee Break**

10:10 AM "Photochemical Reactions of Cyanoacetylene and Dicyanoacetylene: Possible Processes in Titan's Atmosphere"

J.P. Ferris* and J.C. Guillemin

10:30 AM "Controlled Evolution of an RNA Enzyme"

G.F. Joyce*

10:50 AM "Sources and Geochemical Evolution of Cyanide and Formaldehyde"

G. Arrhenius*

11:10 AM "Kaolinite-Catalyzed Air Oxidation of Hydrazine: Considerations of Several Compositional, Structural and Energetic Factors in Surface Activation"

L. Coyne*, R. Mariner and A. Rice

11:30 AM **Lunch**

Co-Chairmen: Robert MacElroy/ Sherwood Chang

1:00 PM "Terrestrial Production vs. Extraterrestrial Delivery of Prebiotic Organics to the Early Earth"

C.F. Chyba*, C. Sagan, P.J. Thomas, L. Brookshaw

1:20 PM "Self Assembly Properties of Primitive Organic Compounds"

D.W. Deamer*

1:40 PM "Structure and Functions of Water-Membrane Interfaces and their Role in Proto-Biological Evolution"

A. Pohorille*, M. Wilson and R. MacElroy

2:00 PM "Macromolecular Recognition: Structural Aspects of the Origin of the Genetic System"

R. Rein*, D. Barak, N. Luo, T. J. Zielinski and M.Shibata

2:20 PM "Template Polymerization of Nucleotide Analogues"

L.E. Orgel*

2:40 PM "Product and Rate Determinations with Chemically Activated Nucleotides in the Presence of Various Prebiotic Materials, Including Other Mono- and Polynucleotides"

A. Kanavarioti*, D.J. Alberas, M.T. Rosenbach, C.F. Bernasconi and S. Chang

3:00 PM **Coffee Break**

3:20 PM "Carbohydrates as a Source of Energy and Matter for the Origin of Life"

A.L. Weber*

3:40 PM "On the Origin and Early Evolution of Biological Catalysis and Other Studies on Chemical Evolution"

J. Oro* and A. Lazcano

4:00 PM	"Chemistry of Aminoacylation of 5'-Amp and the Origin of Protein Synthesis" J.C. Lacey, Jr.*
4:20 PM	"Catalytic RNA and Synthesis of the Peptide Bond" D.A. Usher*, M. Kozlowski and X. Zou
4:40 PM	"New Evidence for a Dramatic Rise in Atmosphere Oxygen ca. 1,900 M.Y. Ago" H.D. Holland* and A.D. Macfarlane
5:00 PM	"Biospheric-Atmospheric Coupling on the Early Earth" J.S. Levine*
5:20 PM	"A Window in Time for the First Evolutionary Radiation" H.J. Morowitz*
5:40 PM	**Adjourn**
6:00 PM	**Poster Session/Reception**

Location: Ames Research Center Cafeteria

Thursday, July 26, 1990

Session IV: Early Evolution of Life

Co-Chairmen: Lawrence I. Hochstein/David J. Des Marais

8:30 AM	"The Effects of Oxygen on the Evolution of Microbial Membranes" L.L. Jahnke*
8:50 AM	"On the Chimerical Nature of the Membrane-Bound ATPase from Halobacterium saccharovorum" L. I. Hochstein*
9:10 AM	"Archaebacterial Rhodopsin Sequences: Implications for Evolution" J.K. Lanyi*
9:30 AM	"Thioredoxin and Evolution" B.B. Buchanan*
9:50 AM	**Coffee Break**

10:30 AM "Exploration of RNA Structure Spaces"

G. Fox*

10:50 AM "Functional Characteristics of the Calcium Modulated Proteins Seen from an Evolutionary Perspective"

R.H. Kretsinger*, S. Nakayama and N.D. Moncrief

11:10 AM "Photosynthetic Reaction Center Complexes from Heliobacteria"

J.T. Trost, W.F.J. Vermaas and R.E. Blankenship*

11:30 AM **Lunch**

Co-Chairman: David J. Des Marais/Lawrence I. Hochstein

1:00 PM "Molecular Bases for Unity and Diversity in Organic Evolution"

S.W. Fox*, P. Ruecknagel and G. Braunitzer

1:20 PM "Sedimentary Organic Molecules: Origins and Information Content"

J.M. Hayes* and K.H. Freeman

1:40 PM "Early Archean Stromatolites: Paleoenvironments Setting and Controls on Formation"

D.R. Lowe*

2:00 PM "Early Archean (~3.4Ga) Prokaryotic Filaments from Cherts of the Apex Basalt, Western Australia: the Oldest Cellularly Preserved Microfossils Now Known"

J.W. Schopf*

2:20 PM "The Environmental Distribution of Late Proterozoic Organisms"

A. Knoll*

2:40 PM "The Biogeochemistry of Microbial Mats, Stromatolites, and the Ancient Biosphere"

D.J. Des Marais* and D.E. Canfield

3:00 PM **Coffee Break**

3:20 PM "Symbiosis and the Origin of Eukaryotic Motility"

L. Margulis* and G. Hinkle

3:40 PM "Is CO_2 Capable of Keeping Early Mars Warm?"

J.F. Kasting*

4:00 PM "Nonmarine Stromatolites and the Search for Early Life on Mars"

S.M. Awramik*

4:20 PM "Endolithic Microbial Model for Martian Exobiology: the Road to Extinction"

E.I. Friedmann and R. Ocampo-Friedmann*

4:40 PM "The NASA Planetary Biology Internship Experience"

G. Hinkle* and L. Margulis

5:00 **Adjourn**

6:30 PM **Banquet**

Location: Garden Alameda Restaurant
Guest Speaker: Carl Sagan "A Small, Blue Dot"

Friday, July 27, 1990

Session V: Evolution of Advanced Life

Chairman: John Billingham

8:30 AM "Fine Structure of the Late Eocene Ir Anomaly in Marine Sediments"

F. Asaro*

8:50 AM "1) Cumulative Frequency Distribution of Past Species Extinctions
2) Geography of Cretaceous Extinctions: Data Base Development"

D.M. Raup*

9:10 AM "The Fossil Record of Evolution: Data on Diversification and Extinction"

J.J. Sepkoski, Jr.*

9:30 AM "Biogeochemical Modeling at Mass Extinction Boundaries"

M.R. Rampino* and K.G. Caldeira

9:50 AM **Coffee Break**

Session VI: SETI

Chairman: Jill Tarter

10:10 AM "The NASA SETI Program"

J. Billingham* and D. H. Brocker

10:30 AM "NASA-SETI Microwave Observing Project - Targeted Search Element"

L.D. Webster*

10:50 AM "NASA SETI Microwave Observing Project - Sky Survey Element"

M.J. Klein*

11:10 AM "The SERENDIP II SETI Project: Current Status"

C.S. Bowyer*, D. Wertheimer, C. Donnelly, W. Herrick and M. Lampton

11:30 AM "Reoptimization of the Ohio State University Radio Telescope for the NASA SETI Program"

R.S. Dixon*

11:50 AM "A Directed Search for Extraterrestrial Laser" Signals"

A. Betz

12:10 PM **Lunch**

Session VII: Solar System Exploration II

Chairman: Glenn C. Carle

1:20 PM "Planetary Protection Issues and Human Exploration of Mars"

D.L. DeVincenzi*

1:40 PM "Analysis of Images Obtained by the Phobos 2 Spacecraft"

W.M. Irvine*

2:00 PM "Titan Aerosol and Gas Experiment for the Huygens Probe"

G.C. Carle*, A. Bar-Nun, M.J. Cohen, J.P. Ferris, J.M. Greenberg, D.R. Kojiro, V. Oberbeck, B.J. O'Hara, J.B. Pollack, T.W. Scattergood and J. Valentin

2:20 PM "Analysis of Model Titan Atmospheric Components Using Ion Mobility Spectrometry"

D.R. Kojiro*, M.J. Cohen, D.E. Humphry, N. Takeuchi, R.F. Wernlund, and R.M. Stimac

2:40 PM "A Silicone Column for GC Analysis of Polar and Nonpolar Chemicals"

T.C. Shen*

3:00 PM "Gas Chromatographic Concepts for the Analysis of Planetary Atmospheres"

J.R. Valentin*, K.W. Hall, R.L. Krekorian, D.K. Cullers and J.B. Phillips

3:20 PM "The Relative Importance of Prebiotic Synthesis on the Earth and Input from Comets and Meteorites"

S.L. Miller*

3:40 PM **Adjourn**

Poster Session
Wednesday, July 25, 1990
6:00 PM - 8:00 PM
Ames Research Center Cafeteria

Presented Abstracts

"Life On Ice: Antarctica and Mars" (Video Presentation)

D. Andersen, C. McKay, R. Wharton, J. Rummel, C. Sagan, S. Squyres and G. Simmons

"Identification and Characterization of Extraterrestrial Non-Chondritic Interplanetary Dust"

D. Blake and R. Fleming

"LDEF Post-Retrieval Analysis in Terms of Exobiology Interests"

T. Bunch, F. Radicati di Brozolo, and R. Fitzgerald

"Recent Spectroscopic Findings Concerning Clay/Water Interactions at Low Humidity: Possible Applications to Models of Martian Surface Reactivity"

L. Coyne, J. Bishop, L. Howard and T. Scattergood

"Crystal-Field-Driven Redox Reactions: How Common Minerals Split H_20 and CO_2 into Reduced H_2 and C Plus Oxygen"

F. Freund, F. Battlo, R. LeRoy, S. Lersky, M. Masuda, and S. Chang

"Kinetics of the Template-Directed Oligomerozation of Guanosine 5'-Phosphate -2-Methylimidazolide: Effect of Temperature on Individual Steps of Reaction"

A. Kanavarioti, C. Bernasconi, and D. Alberas

"Macromolecular Recognition: Structural Aspects of the Origin of the Genetic System"

R. Rein, A. Sokalski, D. Barak, N. Luo, T. Zielenski, and M. Shibuta

"The 2.5 - 5.0 Micron Spectra of IO: Evidence for H_2S and H_2O Frozen in Solid SO_2"

F. Salama, L. Allamandola, F. Witteborn, D. Cruikshank, S.Sanford and J. Bregman

"Laboratory Simulation of the Photoprocessing and Warm-Up of Cometary and Pre-Cometary Ices: Production of Complex Organic Molecules"

W. Schutte, L. Allamandola and S. Sanford

"Biologically Controlled Minerals as Potential Indicators of Life"

D. Schwartz, R. Mancinelli, and E. Kaneshiro

"Photosynthetic Reaction Center Complexes from Heliobacteria"

J. Trost, W. Vermaas, and R. Blankenship

SESSION I

COSMIC EVOLUTION OF BIOGENIC COMPOUNDS

Chairman - T.E. Bunch

Session I consisted of seven papers whose subject material spanned the cosmos from interstellar cloud molecular chemistry to organic compounds found in carbonaceous chondrites.

W. Irvine opened the session with a study of molecular species and their evolution in the environment of interstellar clouds, regions that are the formation sites of stars and, presumably, planetary systems. His recent studies involved the identification of C_4Si, a new carbon chain molecule, astronomically observed in the expelled envelope of an evolved star. This molecule may have formed from the reaction of Si^+ with acetylene and/or aceylene derivatives. His research of cold, dark interstellar clouds has revealed the existence of H_2S, NO, and formic acid. The H_2S abundance may suggest the importance of grain surface synthesis. The observed ratio of ortho- to para-thioformaldehyde, which differs from the theoretical ratio (formed under chemical equilibrium), may suggest efficient interchange between cold dust grains and the gas phase.

Recent advances in the theoretical studies of interstellar molecules by computer were given by D. Defrees. Molecular structure reaction pathways were investigated by using vibrational frequency, molecular property and reaction energy constraints. These were applied to determine spectroscopic constants of candidate interstellar molecules. Accurate predictions of rotational constants and dipole moments of long-chain carbon molecules, $HC^{13}N$, $HC^{15}N$, and C_5O, have been made to aid in determining the size limit of gas-phase interstellar molecules.

R. Saykally and J. Tarter discussed the construction and early results of the new near- to far-IR laser magnetic resonance spectrometer. This instrument was constructed to produce, detect, and characterize carbon cluster spectra. Carbon clusters may account for a large percentage of the circumstellar and interstellar carbon molecular inventory and their relationship to the formation of polycyclic aromatic hydrocarbons (PAHs) may be significant. The technique involves laser evaporation of a graphite target. The resulting clusters are cooled and fed into a spectrometer chamber and resolved at the (near-and) far-IR wavelengths. The technique is a necessary step before carbon clusters can be correctly interpreted in IR spectra taken of the interstellar medium (ISM).

L. Allamandola and colleagues, who are largely responsible for recognizing the importance of and the possible connection of interstellar PAHs to solar system carbon chemistry, reported the results of their success with direct comparsions of astronomic IR spectra of icy objects (ISM grains, comets, and outer planets and satellites) to laboratory analogs. These primordial ices and accompaning complex organics may be preserved in comets, carbonaceous chondrites, and interplanetary dust particles (IDPs). Their method can determine the compared abundances of major constituents of the various ices and place constraints on the types of organics that coat icy grains in the ISM. These materials may have been the basis for solar system biogenic element and compound inventories. They have shown that ices in dense interstellar clouds contain H_2O, CH_3OH, CO, NH_3, and H_2CO as well as nitriles, ketones and esters. Chemical and spectroscopic studies of photolyzed analogs, including deuterated species, are ongoing.

V.G. Anicich and colleagues have been investigating radiation processing of ice surfaces. Radiation causes the formation of radicals in ice which in turn react with other species in the immediate vicinity. Thus, chemistry within the ice could produce complex molecular species by ion-molecule reactions, a scenario that could be viable in comets and other icy bodies. Laboratory results show that when pure ices are radiated with Lyman alpha, an interconversion of CO to CO_2 and CO_2 to CO occurs. In addition, C_3O_2 also forms and this compound has previously been suggested to form in comets by radiation of CO. More complex experiments, together with the study of kinetic factors, are being pursued.

E. Gibson and C. Harmetz have been studing volatiles associated with IDPs by using a laser microprobe-mass spectrometer (LMMS). They analyzed IDPs collected in the stratosphere via U2 aircraft and found a mixture of indigeneous compounds and contaminates (e.g., silicone oil and "cleaning" solvents) associated with the collection techniques. A small fraction of these contaminates remain despite careful "cleaning" attempts, however, spectral-stripping techniques allow for realiable reading of indigeneous compounds. Measured volatiles are similar to those of CI and CM carbonaceous chondrites. Aerogel, a low density material proposed as a passive IDP collection substrate on the Space Station, was also found to contain volatile contaminates from the manufacturing process and these researchers concluded that special efforts will be required to produce "clean" aerogel.

G. Yuen and associates have made long term investigations into the organic chemistry and isotopic composition of the Murchison carbonaceous chondrite. Their present work involves studing the potential of interstellar cloud input of organic matter into the early solar system. They reported from their laboratory experiments that after Murchison acetic acid was decarboxylated and the carbon isotopic composition was measured from the released methane, the isotopic analyses showed sigificant differences in the $^{13}C/^{12}C$ ratios for the methyl and carboxyl carbons of the acetic acid molecule. This strongly suggests more than one carbon source for Murchison organic compounds which has prompted creating laboratory model systems that simulate cosmochemical organic synthesis.

THE CHEMISTRY OF DENSE INTERSTELLAR CLOUDS

W. M. Irvine*
University of Massachusetts

The basic theme of this program is the study of molecular complexity and evolution in interstellar and circumstellar clouds incorporating the biogenic elements. The dense interstellar clouds are the formation sites for stars and presumably for planetary systems. Understanding the molecular composition of these clouds provides probes of physical conditions and evolution by allowing the measurement of local temperature, density and motions; and also provides a means for studying the chemistry in these environments which are so different from those normally encountered in the terrestrial laboratory. Some ninety interstellar molecular species have been identified, the majority of which are organic. The processes producing this chemistry are becoming increasingly well understood, although major questions remain which are being investigated by the observations undertaken as part of this grant.

Recent results include the identification of a new astronomical carbon-chain molecule, C_4Si. This species was detected in the envelope expelled from the evolved star IRC+10216 in observations at the Nobeyama Radio Observatory in Japan. C_4Si is the carrier of six unidentified lines which had previously been observed. This detection reveals the existence of a new series of carbon-chain molecules, C_nSi $(n = 1, 2, 4)$. Such molecules may well be formed from the reaction of Si^+ with acetylene and acetylene derivatives. Other recent research has concentrated on the chemical composition of the cold, dark interstellar clouds, the nearest dense molecular clouds to the solar system. Such regions have very low kinetic temperatures, on the order of 10 K, and are known to be formation sites for solar-type stars. We have recently identified for the first time in such regions the species H_2S, NO, HCOOH (formic acid). The H_2S abundance appears to exceed that predicted by gas-phase models of ion-molecule chemistry, perhaps suggesting the importance of synthesis on grain surfaces. Additional observations in dark clouds have studied the ratio of ortho- to para-thioformaldehyde. Since this ratio is expected to be unaffected by both radiative and ordinary collisional processes in the cloud, it may well reflect the formation conditions for this molecule. The ratio is observed to depart from that expected under conditions of chemical equilibrium at formation, perhaps reflecting efficient interchange between cold dust grains in the gas phase.

THEORETICAL STUDIES OF THE EXTRATERRESTRIAL CHEMISTRY OF BIOGENIC ELEMENTS AND COMPOUNDS

D. J. DeFrees
Molecular Research Institute

Organic compounds, molecules related to those in living systems, are found in many different extraterrestrial environments. Including among these is interstellar space where over 70 molecules have been discovered. The study of organic astrochemistry is important to exobiology both because it demonstrates the ubiquity of processes which led to life on Earth and because the dust clouds where molecules are found are analogs of the solar nebula from which the Earth formed. In the long chain of events leading from the Big Bang, and a universe composed of atomic hydrogen and helium, to the emergence of life on Earth, molecular interstellar clouds are an early link, the most primitive objects which display any significant organic chemistry. One such cloud was the direct precursor to the solar system and to all objects which it contains.

Theoretical methods are ideally suited to studying interstellar cloud chemistry. They have been applied to determine spectroscopic constants of candidate interstellar molecules, mechanisms of ion-molecule reactions, and composition of dust grains. Accurate predictions of rotational constants and dipole moments of long-chain carbon molecules $HC_{13}N$, $HC_{15}N$, and C_5O have been made to aid determining the size limit of gas-phase interstellar molecules. Models of gas-phase interstellar chemistry use reaction rate constants measured at room temperature and extrapolated to interstellar temperatures. The temperature dependence of $NH_3^+ + H_2 \rightarrow NH_4^+ + H$ is anomalous, however, with a minimum rate at about 100K, casting doubt on the extrapolation procedures. The temperature dependence has now been explained.

MEASUREMENT OF THE SPECTRAL SIGNATURE OF SMALL CARBON CLUSTERS AT NEAR AND FAR INFRARED WAVELENGTHS

J.Tarter*
SETI Institute/UC Berkeley Astronomy Department
and
R. Saykally
Chemistry Department, UC Berkeley

A significant percentage of the Carbon inventory of the circumstellar and interstellar media may be in the form of large refractory molecules (or small grains) referred to as carbon clusters. At the small end, uneven numbers of carbon atoms seem to be preferred, whereas above 12 atoms, clusters containing an even number of carbon atoms appear to be preferred in laboratory chemistry. In the lab, the cluster C_{60} appears to be a particularly stable form and has been nicknamed "Bucky Balls" because of its resemblance to a soccer ball and to geodesic domes designed by Buckminster Fuller.

In order to investigate the prevalence of these clusters, and their relationship to the polycyclic aromatic hydrocarbons (PAHs) that have become the newest focus of IR astronomy, it is necessary to determine the spectroscopic characteristics of these clusters at near and far infrared wavelengths. This paper describes the construction of a near to far IR laser magnetic resonance spectrometer that has been built at the University of California Berkeley in order to detect and characterize these spectra. The equipment produces carbon clusters by laser evaporation of a graphitic target. The clusters are then cooled in a supersonic expansion beam in order to simulate conditions in the ISM. The expansion beam feeds into the spectrometer chamber and permits concentrations of clusters sufficiently high as to permit ultra-high resolution spectroscopy at near and far IR wavelengths.

The first successful demonstration of this apparatus occurred last year when the laboratory studies permitted the observational detection of C_5 in the stellar outflow surrounding IRC+10216 in the near-IR. Current efforts focus on reducing the temperature of the supersonic expansion beam that transports the C clusters evaporated from a graphite target into the spectrometer down to temperatures as low as 1°K. If this can be achieved, then the spectral characteristics that are measured in the spectrometer will correctly reflect the physical conditions in the ISM. The first results on the far-IR spectra of C_3 are encouraging. The signal-to-noise ratio is so high that it should be possible to measure the spectral characteristics of much heavier clusters in the near future.

When the lab studies have provided sufficiently precise identifications for these heavier C clusters, an attempt will be made to detect them in circumstellar and interstellar regions using spectrometers flown on the Kuiper Airborne Observatory. The equipment used in these laboratory studies is extremely complicated and difficult to operate, but its advantage lies in the precision with which the various rotational and vibrational transition frequencies can be specified. There can be little or no doubt about subsequent observational identification of astrophysical species.

LABORATORY AND OBSERVATIONAL STUDY OF THE INTERRELATION OF THE CARBONACEOUS COMPONENT OF INTERSTELLAR DUST AND SOLAR SYSTEM MATERIALS

L.J. Allamandola*, S.A. Sanford, W.A. Schutte, and A.G.G.M. Tielens
NASA Ames Research Center

Interstellar dust and gas is the primordial material of the Solar System. Since the Sun and planets formed only some 4.6 billion years ago in a universe thought to be perhaps 15 billion years old, most of the biogenic elements may have already been tied up in complex organic molecules by the time they became incorporated into the planets, asteroids, satellites, and comets. Most interstellar material is concentrated in large molecular clouds where simple molecules are formed by gas phase and dust grain surface reactions. Gaseous species (except H_2) striking the cold (10 K) dust will stick, forming an icy grain mantle. This accretion, coupled with energetic particle bombardment and UV photolysis will produce a complex chemical mixture containing volatile, non-volatile, and isotopically fractionated species. These primordial ices and complex organics may well be preserved without major modification in comets, carbonaceous meteorites, and interplanetary dust particles. By studying the chemical and isotopic composition of interstellar ice and dust, one gains insight into the composition and chemical evolution of the solid bodies in the solar nebula and the nature of the material subsequently brought into the inner part of the solar system by comets and meteorites.

It is now possible to spectroscopically probe the composition of interstellar ice and dust in the mid-infrared, the spectral range which is most diagnostic of fundamental molecular vibrations. We can compare these spectra of various astronomical objects (including the diffuse and dense interstellar medium, comets, and the icy outer planets and their satellites) with the spectra of analogs we produce in the laboratory under conditions which mimic those in these different objects. In this way one can determine the composition and abundances of the major constituents of the various ices and place general constraints on the types of organics coating the grains in the diffuse interstellar medium. In particular we have shown the ices in dense clouds contain H_2O, CH_3OH, CO, perhaps some NH_3 and H_2CO, as well as nitriles and ketones or esters. Furthermore, by studying the photochemistry of these ice analogs in the laboratory, one gains insight into the chemistry which takes place in interstellar/pre-cometary ices. Chemical and spectroscopic studies of photolyzed analogs (including deuterated species) are now underway. The results of some of these studies will be presented and implications for the evolution of the biogenic elements in interstellar dust and comets will be discussed.

QUANTIFICATION OF UV STIMULATED ICE CHEMISTRY: CO AND CO_2

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It has been shown by several investigations in the past that the ice surfaces expected for Oort comets can be processed by various forms of radiation and that new chemical species are formed by the process. The radiation seems to cause the formation of radicals within the ice and then these radicals react with the species present at the boundary of their interstitial sites. Such chemistry within the ice can conceivably produce complex organic compounds by a series of reactions. The continuous radiation of the interstellar molecular clouds has been shown to result in measurable concentrations of complex molecular species by a series of ion-molecule reactions. It seems time to look at the individual reactions that do occur in pure ices and binary mixtures of ices in order to quantify the reactions that occur in icy bodies.

Recent laboratory experiments are presented that show that during photolysis of the pure ices there is evidence of the interconversion of CO to CO_2 and CO_2 to CO using Lyman alpha (1216Å) radiation. In addition, there is a substantial amount of another substance being produced. This substance is evident by its infrared absorption peak at 2235 cm^{-1}. It is believed that this new peak is due to carbon suboxide, C_3O_2. CO and CO_2 have already been detected in comets, and C_3O_2 has been suggested as a cometary from radiation of CO [Delitsky and Huntress, *BAAS* **20**, (1988)]. Comparisons are made between our results at 1215Å and proton radiation experiments and radiation at other wavelengths. The suggestion is that the processing of ices is energy dependent, i.e. dependent on the type of radiation. Several difficult problems have to be solved before these radiation conversion can be quantified. The steps that we are taking to quantify the kinetics are discussed.

VOLATILES IN INTERPLANETARY DUST PARTICLES AND AEROGELS

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Interplanetary dust particles (IDPs) offer a unique opportunity for developing a better understanding of the cosmic history of the organogenic elements. The study of IDPs has shown that they are complex, heterogeneous assemblages of both high and low temperature phases and minor amounts of amorphous components. Some components in IDPs may have originated as stellar or nebular condensates, interstellar dust, interstellar or nebular molecules and products of parent body processes (e.g. on comets or asteroids). The degree of success in distinguishing between these possible sources rests largely with the ability to carry out compositional analysis for elemental, isotopic, molecular, and mineralogical characterization. We have been studying the nature of volatiles associated with IDPs by analyzing the materials associated with the collection of IDPs (i.e. silicone oil, etc.) along with analyzing individual IDPs which have been "cleaned of their contaminants." A laser microprobe-mass spectrometer (LMMS) technique is utilized to vaporize the volatiles within an individual IDP and detect the components associated with the particle.

Volatiles measured in 25 IDPs are a mixture of both indigenous materials and contaminants associated with the collection and processing of the IDPs prior to analysis. Most IDPs have been collected in the stratosphere using a silicone oil/ freon mixture (20:1 ratio) coated on collector plates. Studies have shown that silicone oil, freon and hexane residues remain with the IDPs, despite attempts to clean the IDPs. Analysis of the IDPs with the LMMS-technique produces spectra with a mixture of indigeneous and contaminants components. Contamination signal can be identified and removed, however the contamination signal may obscure some of the indigeneous component's signal. Employing spectra stripping techniques, the indigenous volatile constituents associated with the IDPs can be identified. Volatiles are similar to those measured in CI or CM carbonaceous chondrites. Collection of IDPs in low-Earth orbit utilizing a Cosmic Dust Collection Facility attached to Space Station Freedom has been proposed. The low-density material aerogel has been proposed as a collection substrate for IDPs. Our studies have concentrated on identifying volatile contaminants that are associated with aerogel. We have found that solvents used for the preparation of aerogel remain in aerogel and methods must be developed for removing the entrapped solvents before aerogels can be used for an IDP collection substrate.

ISOTOPIC COMPOSITION OF MURCHISON ORGANIC COMPOUNDS: INTRAMOLECULAR CARBON ISOTOPE FRACTIONATION OF ACETIC ACID.

SIMULATION STUDIES OF COSMOCHEMICAL ORGANIC SYNTHESES.

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and
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During the last 20 years, the organic compounds of the Murchison meteorite and, to a lesser extent, other carbonaceous chondrites have been the object of extensive qualitative and quantitative analyses. These data provide a detailed record of the formation of organic compounds in the early solar system. Recent stable isotope analyses, especially deuterium analyses, suggest that the meteorite organics are closely related to, although not identical to, interstellar organic compounds. The meteorite organics appear to have been derived from interstellar precursors during hydrothermal alteration of the meteorite parent body. Meteorites, as well as comets, may have been essential carriers of organic compounds to planetary bodies in the habitable (liquid water) zone of the solar system. The organic compounds of carbonaceous chondrites seem to provide evidence for a relationship between the massive organic content of interstellar clouds and the organic-rich environment that is presumably necessary for the origin of life on a planetary body. Further characterization of the organic components of these meteorites is essential to understanding organic chemical evolution in the early solar system. Research in progress is aimed at (i) acquisition of additional qualitative and quantitative data concerning meteoritic hydrocarbons, amines, amino acids, amino acid precursors, and carboxylic acids, (ii) determination of the stable isotope content of these compounds, (iii) comparison of isomeric variation and isotopic content in the meteorite compounds with that found in the synthetic products from model processes, and (iv) relating organic compounds to specific mineral phases of the meteorite matrix. These data will further illuminate the origin of meteorite organic compounds and their relationships to interstellar organics and other solar organic matter, for example, that of comets and interplanetary dust particles (IDPs).

Recently, in our laboratories, samples of Murchison acetic acid were decarboxylated successfully and the carbon isotopic composition was measured for the methane released by this procedure. These analyses showed significant differences in $^{13}C/^{12}C$ ratios for the methyl and carboxyl carbons of acetic acid molecule - strongly suggesting that more than one carbon source may be involved in the synthesis of the Murchison organic compounds. On the basis of this finding, laboratory model systems simulating cosmochemical synthesis are being studied, especially those processes capable of involving two or more starting carbon sources.

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SESSION II

SOLAR SYSTEM EXPLORATION (I)

Chairman - R. L. Mancinelli

The primary focus of Session II centered around methods for the search for traces of an extinct martian biota. A variety of papers were presented ranging from the design of flight hardware to conduct experiments of interest to exobiology in interstellar space, to speculation on the presence of life on Mars.

P. Tsou spoke on the intact capture of cosmic dust particles traveling at hypervelocities using a newly developed, light weight, inorganic silicate dust "catcher" termed aerogel. In addition to being an efficient collector of small particles, aerogel decreases the possibility of contamination of samples with extraneous organic material.

J. Huntington presented the concept of the Space Station's gas grain facility and explained some of the potential applications for exobiology. J. Marshall explained the use of the Space Shuttle "Glove Box Experiment", conceived and designed by him to study the physics of particle aggregation in microgravity. This self-contained experimental facility is scheduled to be flown and tested on the Shuttle during March of 1992. The glove box microgravity research facility is being built by ESA and, once fully developed, will be operated on a continuous basis and available to the scientific community at large.

The concept of using laser spectroscopy to determine the ratio of ^{13}C to ^{12}C in martian samples during a Mars mission was presented by Todd Sauke. He and co-author J. Becker concluded that the 2300 cm^{-1} spectral region is the ideal portion of the spectra in which to make these measurements. This was based on the fact that the rotational lines of the two carbon isotopes in this region have approximately equal absorbance at the isotopic ratios of the two isotopes as they occur on Earth and in the martian atmosphere. Using sweep integration and signal averaging techniques, they have measured the stable isotope ratio of CO_2 samples to better than 1%, and strive to a precision better than 0.1%.

J. Orenberg presented a model of the reflectance spectral data in the UV/VIS/NIR 0.3 to 2.5 mm-region and the IR 2.5 to 25 mm-region illustrating that the martian surface material may be composed of palagonites and 2 to 4% clays. T. Roush presented data from the recent airborne thermal infrared observation of Mars from the Kuiper Airborne Observatory which provided evidence for the presence of carbonates, sulfates, and hydrates in the dust in the atmosphere of Mars.

R.A. Wharton presented data regarding the applicability of perennially frozen lakes as model systems for studying the possible evolution of life on Mars. In particular, he discussed the mechanism of supersaturating the water beneath the icecover with N_2 and O_2 from the atmosphere, and how this may have benefited a possible martian biota as Mars lost its atmosphere and became colder and drier. He also discussed the mechanisms by which sediment enters the lakes through cracks in the ice.

P.J. Boston presented a summary of the current speculation regarding the possibility of life existing beneath the surface of Mars. She stated that buried organisms would be protected from the harsh conditions of the planet's surface, and that such habitats could receive geothermal heat and so maintain water in a liquid state. In addition, geothermally or volcanically reduced gases from the planet's interior could provide the reducing power needed for a closed or semi-closed microbial ecosystem to survive.

R.L. Mancinelli presented data on carbon and nitrogen cycling in simple microbial communities. Using these data, he showed that one can define experiments and put limits on the types and kinds of compounds that may be utilized as martian paleobiomarkers (i.e. traces of an extinct martian biota). In addition, these results provide a database for ecological data interpretation enabling one to distinguish abiotic from biotic processes on Mars. In particular, he presented data demonstrating that *Synechococcus nägeli 1849* while housed within a mixed gypsum halite crust was actively dividing and was obtaining its carbon and nitrogen from atmospheric CO_2 and N_2 respectively, through carbon and nitrogen fixation. This was presented as a possible scenario for a current martian "oasis" or a last refuge as the planet lost its atmosphere and became cold and dry. In addition, he presented data from a "strawman" Mars soil analysis experiment defined from the database gathered from the ecological studies of simple microbial communities. This "strawman" experimental design illustrated how one can identify organic matter in soil and gypsum halite evaporites using differential thermal analysis and gas chromatography.

A. Zent presented a strawman conceptual design for the analysis of the oxidation potential of the martian surface. For example, he proposed that acetonitrile be used in place of water as a solvent for measuring the Eh of the martian surface material using an Eh electrode.

INTACT CAPTURE OF COSMIC DUST

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Cosmic dust are extraterrestrial particles of cometary, asteroidal, samples of planetesimals or even interstellar origin. Capturing these particles and returning them to Earth so that they can be individually analyzed will contribute to our understanding of the origin and evolution of our solar system. Dust analyses include elemental, isotopic, and organic compositions and morphologic, petrographic, and phase studies. The precision of the measurements and the range in sizes of analyzed particles will exceed what can be done with in situ techniques on any space flight missions. Furthermore, when particles can be captured intact without melting, then biological elements and compounds and especially the original structural and phase characteristics of the material can be preserved. This information is important to the study of the cosmic evolution of biogenic compounds and the development models for prebiotic and biotic evolution.

The encounter speeds of cosmic dust in Earth orbit are at hypervelocities. It was believed that hypervelocity particles could not be captured intact; thus, the use of capture cell or atomized capture of cosmic dust. The focus of this development effort is to capture dust particles at hypervelocities intact, unmelted to preserve even volatile organics, at the same time the capture process must minimize any organic elemental or compound contamination to prevent any compromise of exobiological analyses. Inorganic silicate aerogel has been developed as a successful capture medium to satisfy both requirements of intact capture and minimal organic contamination. Up to 6 km/s, silicate projectiles from few microns up to 100 µm have been captured intact without any melting and with minimal loss of mass. Carbon in silicate aerogel can be reduced to less than 1 part in 1000 and hydrogen 3 parts in 1000 when baked in air. Under controlled inert gas environments additional hydrocarbon reduction can be achieved.

EXOBIOLOGICAL IMPLICATIONS OF DUST AGGREGATION IN PLANETARY ATMOSPHERES: AN EXPERIMENT FOR THE GAS-GRAIN SIMULATION FACILITY

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Processes involving small particles (micrometer to centimeter in size) are important to the understanding of a wide diversity of phenomena. Among them is the tendency for very fine particles (dust) to aggregate into clusters as a result of surface electrostatic charging and van der Waals forces, for example. Clustering or aggregation of materials has played an important role in the origin and evolution of life. Within our own solar system, this aggregation process influenced the rate and mode of formation of the solar system bodies themselves; it has continued to influence life by controlling the rate at which planetary atmospheres are cleansed of dust palls.

Aggregation of fine particles has been extensively modeled by mathematical analysis and computer simulations, but the study of such phenomena in the terrestrial laboratory is virtually impossible due to the fact that aggregation causes rapid sedimentation of materials to the bottom of the experimental chamber; there is insufficient time for aggregates to fully develop, and there is insufficient time for studying their behavior. This problem can be overcome by conducting experiments in microgravity where protracted suspension times can be achieved. The Gas-Grain Simulation Facility (GGSF) will provide such a microgravity environment where undesirable environmental effects are reduced, and thus, experiments involving interactions between small particles and grains can be more suitably performed.

The GGSF will occupy a Space Station double rack and consist of a number of subsystems supporting an experiment chamber. The subsystems will provide environmental control (to regulate temperature, pressure, humidity, etc.), mechanisms for injecting and removing particles and clouds of particles, levitation systems, shock mounts and other vibration-isolating systems, energy sources, and a number of experiment monitoring and measuring devices. A number of experiments spanning a range of disciplines have been proposed for performance in the GGSF which will be flown in several phases until the year 2000 when it will be a fully independent module onboard Space Station Freedom.

The earliest flight opportunity is the ESA glovebox facility onboard Shuttle. Slated for flight in 1992, this glovebox will serve as a scientific and technological testbed for GGSF exobiology experiments as well as generating some basic scientific data. Initial glovebox experiments will test a method of generating a stable, mono-dispersed cloud of fine particles using a vibrating sprinkler system. In the absence of gravity and atmospheric turbulence, it will be possible to determine the influence of interparticle forces in controlling the rate and mode of aggregation. The experimental chamber can be purged of suspended material to enable multiple repetitions of the experiments. Of particular interest will be the number of particles per unit volume of the chamber because it is suspected that aggregation will occur extremely rapidly if the number exceeds a critical value. All aggregation events will be recorded on high-resolution video film. Changes in the experimental procedure as a result of surprise events will be accommodated by real-time interaction with the mission specialist during the Shuttle flight.

STABLE CARBON ISOTOPE MEASUREMENTS USING LASER SPECTROSCOPY

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On Earth, autotrophic organisms incorporate carbon-12 into their bodies with greater efficiency than carbon-13. Carbon in organic earth sediments is enhanced in ^{12}C by about 2-3% and this enhancement constitutes a striking signature of the presence of life. The ability to measure $^{12}C/^{13}C$ ratios *in situ* would represent a powerful discriminatory tool for searching for now-extinct life on Mars which may have laid down isotopically enhanced carbon deposits. A Mars Rover and Sample Return mission could utilize a carbon isotopic ratio measurement to help select which rocks and soil samples to bring back to Earth and which to discard. Lead-salt tunable diode lasers (TDLs) emit coherent infra-red light with a very narrow linewidth of approximately 0.0003 cm^{-1}. It is possible to use a TDL to measure individual rotational lines within the vibrational absorption band and determine their intensities, which can be used to determine gas concentration and carbon isotopic ratios of CO_2 derived from Martian rock and soil samples.

The 2300 cm^{-1} spectral region is especially interesting because the $^{12}CO_2$ and $^{13}CO_2$ bands overlap in such a way that their rotational lines have approximately equal absorbance at the anticipated isotopic ratio (~90) of carbon on Earth and Mars. Pairs of rotational lines we have studied are separated by as little as 0.050 cm^{-1}, but are well resolved with a TDL. Using sophisticated sweep integration and signal averaging techniques, we have measured the stable isotope ratio in carbon dioxide to a precision of better than 1%.

PALEOLAKES AND LIFE ON EARLY MARS

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Did life begin on early Mars, as it did on Earth, during the planets' first billion years after accretion? Early Mars had volcanism, an atmosphere, and liquid water - the essential ingredient for life as we know it. Knowing whether or not life existed on Mars is fundamental to our understanding of how life began in our solar system. During future Mars missions, the search for evidence of extinct life can be directed by research of terrestrial analogs of the possible conditions on Mars as the planet became cold and dry. The McMurdo Dry Valleys in Antarctica have a mean annual temperature of -20°C and less than 10 mm precipitation, yet within this barren land, perennially ice-covered lakes harbor rich communities of microbial mats, cold-water homologs of ancient stromatolitic communities. The translucent ice-cover insulates the subsurface liquid water from a frigid environment and permits photosynthetic microorganisms to proliferate. In addition, atmospheric gases are concentrated well above saturation by the exsolution of gases during freezing and the subsequent loss of water through sublimation. These results suggest that the purported Martian lakes, such as in Valles Marineris, may have harbored and extended the time period for life by providing light, liquid water, and concentrated gases as Mars cooled and its atmosphere thinned.

Two research directions have begun to elucidate key parameters in the search for extinct life on Mars. Carbonate sediments, deposited about 10,000 years ago in association with biological activity, have been sampled from the paleolake beds of Lake Vanda and Meirs in the McMurdo Dry Valleys. These samples are being analyzed for simple biological signatures that remain in cold and dry paleolake sediments, namely microfossils, percent carbonate, and total organic carbon. Our second initiative is the study of Colour Lake, in the Canadian Arctic, that periodically maintains a perennial ice-cover. Physical measurements started this year will be used to determine one end-point for ice-covered lake environments and will be compared to continuous measurements from Antarctic lakes started in November 1985. Interestingly, Colour Lake also supports benthic mat communities but the low pH precludes carbonate deposition. This research will broaden our knowledge base for what conditions are necessary for ice-covered lake formation and what biological signatures will remain in paleolake deposits.

SUBSURFACE MICROBIAL HABITATS ON MARS

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and
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We have developed scenarios for shallow and deep subsurface cryptic niches for microbial life on Mars. Such habitats could have considerably prolonged the persistence of life on Mars as surface conditions became increasingly inhospitable. The scenarios rely on geothermal hot spots existing below the near or deep subsurface of Mars. Recent advances in the comparatively new field of deep subsurface microbiology have revealed previously unsuspected rich aerobic and anaerobic microbial communities far below the surface of Earth. Such habitats protected from the grim surface conditions on Mars could receive warmth from below and maintain water in its liquid state. In addition, geothermally or volcanically reduced gases percolating from below through a microbiologically active zone could provide reducing power needed for a closed or semi-closed microbial ecosystem to thrive.

Sulfur is such an abundant element in the surface materials of Mars that one might expect this element to be abundant in subsurface material as well. Sulfur in its many forms should be readily available to enter into the microbial chemistry of a subsurface Martian ecosystem. To begin to substantiate the plausibility of our scenarios, we are conducting preliminary experiments on several pure cultures and samples from natural sulfureta to investigate the minimum concentrations of H_2S which can be used in various metabolic processes by these organisms.

Scenario development of possible Martian habitats of the past or present is difficult in light of our limited knowledge of the planet. Nevertheless, such development is critical for designing future robotic and human expeditions to look for extant life or traces of extinct life. The subsurface habitats we suggest are amenable to the new microbial drilling technologies being developed in the field of deep subsurface microbiological remediation of subsurface pollutants. Techniques which will recover microbiologically uncompromised deep samples for biological analysis will also provide a wealth of information for Martian geologists, hydrologists, and volcanologists to ponder.

PALEOBIOMARKERS AND DEFINING EXOBIOLOGY EXPERIMENTS FOR FUTURE MARS EXPERIMENTS

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Mars is a cold, dry planet with an oxidizing surface bombarded by ultraviolet and ionizing radiation making prospects for an extant Mars biota bleak. Yet, it is suggested that early earth and early Mars were similar enough that life may have evolved on Mars. If life did evolve on Mars, what evidence for its existence might we find, that is, what constitutes a Martian paleobiomarker, and how can we distinguish such a marker from abiotically produced substances? The topics studied to answer this question include carbon and nitrogen cycling, as well as the stability and relative abundance of their intermediates in microbially dominated ecosystems. The microbially dominated ecosystems studied are the cryptoendolithic microbial community living within sandstone rocks, endoevaporite microbial community living inside salt crystals, and the microbial mat communities living beneath perennially ice-covered lakes and hypersaline ponds. The nitrogen cycle of these communities ranges from the simple, where only assimilation occurs (e.g., cryptoendoliths and endoevaporites) to the more complex where a complete cycle occurs (e.g., microbial mats). The carbon cycle of these communities appears to be complete that is, carbon fixation and remineralization through respiration occur.

The nitrogen cycle of the cryptoendolithic community, composed primarily of a lichen, inhabiting the Antarctic dry valleys, is incomplete. Biological nitrogen fixation, denitrification and nitrification do not occur in nature within this community. All of the fixed nitrogen is supplied exogenously. This is much like the nitrogen cycle of the endoevaporitic microbial community inhabiting a natural mixed crust of halite and gypsum. The endoevaporite community consists primarily of a cyanobacterium tentatively identified as a member of the genus *Synechococcus* Nägeli 1849. *In situ* measurements demonstrate that this community fixes nitrogen in nature, but neither nitrification nor denitrification was detected. The microbial community inhabiting these ecosystems perform the least number of transformations of nitrogen of any ecosystem reported to date, and therefore may represent the simplest nitrogen cycle in nature. Both of these communities, however, fix carbon photoautotrophically.

In contrast, benthic microbial mats carry out complete nitrogen and carbon cycles in nature. The mat inhabiting Lake Hoare, a perennially ice-covered lake in Taylor Valley, Antarctica exhibits an incomplete nitrogen cycle during the austral summer (no N_2-fixation), and a complete nitrogen cycle during spring before melt water runs into the lake. These data suggest that the demand for nitrogen is being met by input from meltwater and sediment entering the lake. Denitrification occurs only within anaerobic sediments, whereas nitrification only occurs in the aerobic portions of the sediment and mat. In the microbial mats inhabiting a hypersaline pond, the nitrogen cycle appears to always be complete. The pattern of nitrogen and carbon fixation and denitrification varies diurnally. Data suggests that this phenomenon is due to diurnal changes in nutrient limitation.

These studies allow us to define experiments and put limits on the types and kinds of compounds that may be utilized as Martian paleobiomarkers. In addition, they provide a data base for ecological data interpretation enabling us to distinguish abiotic from biotic processes.

CONCEPTUAL DESIGNS FOR IN SITU ANALYSIS OF MARS SOIL

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and
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The Viking Biology results, and the absence of organic material in the soil of Mars have led to the suggestion that there is one or more oxidants in the martian soil. Based upon the results of the Gas Exchange Experiment and the Labeled Release Experiment, Klein (Icarus, **34**, 666, 1978) suggested the presence of three oxidants: a strong thermally stable oxidant, a strong thermally labile oxidant, and a weak oxidant.

The nature and concentration of oxidants in the martian soil has two important implications: for exobiology, the preservation of organic material from an early biological period on Mars; and for human exploration, the health and safety of astronauts on the surface. As indicated by the absence of organic material in the near surface at the two Viking sites, the oxidant may have destroyed any organic material to some depth. The depth from which samples must be returned if there is to be any hope of finding organic material on Mars will depend on the nature of the soil oxidants and their mobility through the soil. For human explorers the soil oxidant may pose a hazard to material and equipment as well as a health hazard due to the inevitable movement of dust within the habitat.

The goal of this research is to develop conceptual designs for instrumentation to perform in situ measurements of the Martian soil in order to determine the existence and nature of any reactive chemicals.

Our approach to this problem involves three aspects: 1) Assessment and critical review of the Viking Biology results which indicated the presence of a soil oxidant. 2) An investigation of the possible application of standard soil science techniques to the analysis of Martian soil. 3) Preliminary consideration of non-standard methods that may be necessary for use in the highly oxidizing Martian soil.

Based on our preliminary analysis we have developed strawman concepts for standard soil analysis on Mars, including pH, suitable for use on a Mars rover mission. In addition, we have devised a method for the determination of the possible strong oxidants on Mars.

SPECTROSCOPY AND REACTIVITY OF MINERAL ANALOGS OF THE MARTIAN SOIL

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and
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In order for exobiologists to gain a better understanding of the similarities and differences between the early environments on Earth and Mars, and thus to answer a primary question in comparative planetology as to why life developed on earth to its rather complex level and why, apparently, this did not occur on Mars, the geochemical and physical aspects of the martian soil must be studied and elucidated, The martian soil participates in present day surface-atmosphere interactions, volatile balances, and geological land forming processes. The soil holds important clues to the processes that shaped the early geological history of Mars, to the amount of liquid once present, and to the possibility of early evolved life or existing life on the planet.

Some of the "best" Mars analog mineral models of the soil have been prepared and justified according to known constraints of chemical composition, reflectance spectroscopy and chemical reactivity. Detailed laboratory reflectance spectra in the UV/VIS/NIR (.30-2.5 μm) and IR (2.5-25 μm) regions have been obtained for the pure candidate minerals and some analog mixtures and compared to Mars reflectance spectra. Modeling of the reflectance spectra from optical constants determined for the analog minerals has begun and will be interpreted in terms of the effects of particle size variation, component mixing, and soil packing upon remotely sensed reflectance spectra. This has implications not only for Mars, but for other planets and planetoids. The ratio of Fe(II)/Fe(III) in the martian soil analog materials on spectral reflectance in the visible range has begun, and the results will be evaluated according to conformity with the visible Mars reflectance spectrum. Some initial LR and GEX data have been collected for the mineral samples and their mixtures which can be compared to the Viking data and interpreted in terms of the redox (Fe(II)/Fe(III) environment.

MIDINFRARED SPECTRAL INVESTIGATIONS OF CARBONATES: ANALYSIS OF REMOTELY SENSED DATA

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There are ample theoretical reasons and geomorphic evidence that during the earliest history of Mars liquid water was stable at the surface. The higher temperatures required to maintain water as a liquid are often attributed to higher concentrations (1-10 bars) of the greenhouse gas carbon dioxide (CO_2). The current observed concentration of CO_2 (roughly 7 mbars) leads to an enigma regarding the fate of the remaining original gas. One line of reasoning suggests that CO_2 reacted chemically with igneous silicates to form carbonate (CO_3) rocks, resulting in its permanent removal from the atmosphere. If this scenario is correct, then identification of CO_3 rocks on the current martian surface would provide evidence of an early clement environment where the presence of higher temperatures and liquid water may have been conducive to the evolution of life. Additionally, identification of specific CO_3 species can provide significant insight into the depositional environment in which they formed.

Recent airborne thermal infrared observations of Mars from the Kuiper Airborne Observatory (KAO) have provided evidence for the presence of carbonates, sulfates (SO_4), and hydrates. Analyses of these data have relied upon radiative transfer models which account for thermal emission from the surface, as well as absorption, emission and scattering due to both solids and gases present in the atmosphere. From first principals these models rely upon knowledge of the optical properties of materials, and these are limited for CO_3's and SO_4's. While the optical properties of calcite ($CaCO_3$) and anhydrite ($CaSO_4$) can not explain the details of specific spectral features, values of more appropriate materials are unavailable. Using the optical properties of calcite and anhydrite, it was estimated that CO_3's and SO_4's constituted about 1-3 and 10-15 wt.%, respectively of the materials composing the atmospheric dust. Using the derived value as an estimate of total CO_3 abundance, and making an assumption that the CO_3's were uniformly distributed within the martian regolith, it was estimated that such a CO_3 reservoir could contain roughly 2-5 bars of CO_2.

While the results indicate that several volatile-bearing materials are present on Mars, the observations from the KAO are inherently limited in their ability to determine the spatial distribution of these materials. However, previous space craft observations of Mars provide both the spectral coverage necessary to identify these materials, as well as the potential for investigating their spatial variability. This has prompted us to pursue a reinvestigation of the Mariner 6 and 7 infrared spectrometer and Mariner 9 infrared interferometer spectrometer observations. The former data have been recently made available in digital format and calibration of wavelengths and intensities are almost complete. Additionally, we are pursuing the derivation of optical constants of more appropriate carbonates and sulfates.

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SESSION III

PREBIOTIC EVOLUTION

Chairman - S. Chang

Session III covered a wide range of topics in prebiotic evolution and the origin of life. In the twenty one papers presented, the topics ranged from the origin of organic matter in meteorites and the outer planets to nucleic acid polymerization and evolution on the early Earth to the rise of oxygen in the Proterozoic.

J. Kerridge started the session by summarizing the status of isotopic studies of the organic matter in carbonaceous meteorites in a paper entitled "Isotopic Constraints on the Origin of Meteoritic Organic Matter." He pointed out the importance of isotopic measurements of carbon, nitrogen and hydrogen in elucidating the origin and synthetic pathways for the organic components, and he described his progress in developing secondary ion mass spectrometry as a technique for measuring hydrogen isotopic compositions of specific molecular fractions. Anomalously high ratios of D/H which have been observed in organic extracts from meteorites have been attributed to interstellar origins.

In "Kinetic Conversion of CO to CH_4 in the Solar System," Y. Yung, M. Allen, and J. Pinto described theoretical calculations showing the importance of formation of the methoxy radical, CH_3O, in the conversion of CO to CH_4. They discussed the possible relevance of various steps in the overall process to organic synthesis in the Earth's early atmosphere, to chemical evolution of carbon in the solar nebula and to putative evidence for polyoxymethylene in comet Halley.

The next three papers described laboratory simulations of organic chemical processes in the outer solar system. "Production of Organic Compounds in Plasmas: a Comparison Among Electric Sparks, Laser-induced Plasmas and UV Light," summarized work by T. Scattergood, C. McKay, W. Borucki, L. Giver, H. Van Ghyseghem, J. Parris, and S. Miller. This team showed that ultraviolet photochemistry resulting from light produced in spark and plasma processes was responsible for the synthesis of saturated hydrocarbons in excess of those predicted by theory. Results of experiments on plasma excitation of simulated planetary atmospheres and charged particle irradiation of mixtures of hydrocarbon and water ices as analogs of icy bodies were described by C. Sagan, W. Thompson, B. Khare, and C. Chyba in the paper, "Organic Synthesis in the Outer Solar System: Recent Laboratory Simulations for Titan, the Jovian Planets, Triton and Comets." The plasma experiments were able to account for all species observed by the Voyager spacecraft at Titan, and the ice irradiations afforded product mixtures whose IR spectra contained a band at 3.4 m matching the emission feature of Comet Halley and other comets. J. Ferris and J. Guillemin reported on "Photochemical Reactions of Cyanoacetylene and Dicyanoacetylene: Possible Processes in Titan's Atmosphere." These authors described the production of cyanobenzenes and cyanocyclooctatetraenes and suggested a synthesis mechanism involving cyanocyclobutadienes as intermediates. The findings of all three papers underscored the rich organic chemistry that may be found in the atmospheres and surface materials of objects in the outer solar system.

A transition in chemical evolution from the outer to the inner planets was provided by two papers. The first was that of C. Chyba, C. Sagan, P. Thomas, and L. Brookshaw on " Terrestrial Production vs. Extraterrestrial Delivery of Prebiotic Organics to the Early Earth." These workers conducted a theoretical study of the interaction of impacting comets/asteroids with Earth's early atmosphere and surface. In their evaluation of endogenic versus exogenic processes, they concluded that the contribution of organic compounds delivered intact by comets would have exceeded those provided by asteroidal impacts, interplanetary dust particles or atmospheric synthesis in scenarios calling for a dense CO_2 atmosphere. The second paper on "Self-Assembly Properties of Primitive Organic Compounds" was given by D. Deamer. He showed that pyrene, a major polycyclic aromatic hydrocarbon found in the Murchison meteorite, acted as a photosensitizer in the aqueous photochemical hydroxylation of hydrocarbons to produce surface active molecules which could have been capable of participating in membrane formation on the primitive Earth.

In theoretical studies relevant to primitive membrane formation and function, A. Pohorille, M. Wilson, and R. MacElroy investigated the "Structure and Functions of Water-Membrane Interfaces and Their Role in Proto-biological Evolution." In computer simulations, these researchers showed that the dipolar orientation of water at nonpolar interfaces facilitates the approach of positive rather than negative ions and that amphiphilic molecules also take a preferred orientation such that the polar group is buried in the water while the hydrocarbon portion extends into the nonpolar medium. Their model studies have also revealed that simple ionophores bind and transport ions by the same physical chemical mechanism as do ion channels and carriers from modern cells.

The next series of papers discussed additional aspects of chemical evolution on the Earth. In the first, "Sources and Geochemical Evolution of Cyanide and Formaldehyde," delivered by G. Arrhenius, synthesis of cyanide by deposition of auroral electrons into a CO_2-containing atmosphere was hypothesized. Literature data and experimental results suggested that cyanide could have been preserved against hydrolysis in the form of inorganic ferrocyanide and released by photooxidation of the latter, followed by reactions with formaldehyde to form glycolonitrile and other products of interest for chemical evolution. The role of inorganic material in chemical evolution was also the subject of the paper by L. Coyne, R. Mariner, and A. Rice entitled "Kaolinite-catalyzed Air Oxidation of Hydrazine: Consideration of Several Compositional, Structural, and Energetic Factors in Surface Activation." Using hydrazine oxidation as a reaction to investigate the energy sources and identity of various types of catalytic sites in clay, these workers showed that O^- centers and ferric iron centers play dominant roles rather than simply trace structural and surface contaminants. Energy was also the focus of "Carbohydrates as a Source of Energy and Matter for the Origin of Life" by A. Weber who reported recent developments in his model for early glycolysis including racemization-free thermal synthesis of polyglyceric acid and determination of the free energy available through hydrolysis of its 2- and 3-glyceryl esters. Weber also reported that glyceraldehyde is bound and oxidized to glyceric acid on ferric hydroxide surfaces while soluble ferric iron catalyzes the rearrangement of glyceraldehyde to lactic acid.

ISOTOPIC CONSTRAINTS ON THE ORIGIN OF METEORITIC ORGANIC MATTER

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Salient features of the isotopic distribution of H, C and N in the organic material found in carbonaceous meteorites are the following: Most organic fractions are strongly enriched in D with respect to the D/H ratio characteristic of H_2 in the protosolar system; substantial variations in $^{13}C/^{12}C$ ratio are found among different molecular species, with oxidised species tending to be ^{13}C-enriched relative to reduced species; some homologous series reveal systematic decrease in $^{13}C/^{12}C$ with increasing C number; considerable variation in $^{15}N/^{14}N$ ratio is observed within organic matter, though no systematic pattern to its distribution has yet emerged; no interelement correlations have been observed between isotope enrichments for the different biogenic elements. The isotopic complexity echoes the molecular diversity observed in meteoritic organic matter and suggests that the organic matter was formed by multiple processes and/or from multiple sources. However, existence of a few systematic patterns points towards survival of isotopic signatures characteristic of one or more specific processes. The widespread D enrichment implies either survival of many species of interstellar molecule or synthesis from a reservoir containing a significant interstellar component.

Several of the questions raised above can be addressed by more detailed determination of the distribution of the H, C and N isotopes among different well-characterised molecular fractions. Thus, the present study is aimed at discovering whether the different amino acids have comparable D enrichments, which would imply local synthesis from a D-enriched reservoir, or very variable D enrichments, which would imply survival of some interstellar amino acids. The same approach is also being applied to polycyclic aromatic hydrocarbons. Because the analytical technique employed (secondary ion mass spectrometry) can acquire data for all three isotopic systems from each molecular fraction, any presently obscured interelement isotopic correlation should also be revealed, which will aid in identifying pertinent synthetic processes.

KINETIC CONVERSION OF CO TO CH_4 IN THE SOLAR SYSTEM

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Some of the most interesting chemistry in the Solar System involves changes in the oxidation state of the simple carbon species. The chemical pathways for the conversion of CH_4 to CO and CO_2 are for the most part known. The reverse process, the reduction of CO to CH_4, is, however, poorly understood. This is surprising in view of the importance of the reduction process in the chemistry of the Solar System. Recently we investigated the chemical kinetics of a hitherto unsuspected reaction. It is argued that the formation of the methoxy radical (CH_3O) from $H+H_2CO$ may play an essential role in the reduction of CO to CH_4. The rate coefficient for this reaction has been estimated using the approximate theory of J. Troe and transition state theory. We will discuss the implications of this reaction for the chemistry of CO on Jupiter, in the solar nebula, for interpreting the laboratory experiments of A. Bar-Nun and A. Shaviv and A. Bar-Nun and S. Chang and for organic synthesis in the prebiotic terrestrial atmosphere. The possible relation of CO reduction in the solar nebula and polyoxymethylene observed in comet Halley will be discussed.

PRODUCTION OF ORGANIC COMPOUNDS IN PLASMAS: A COMPARISON AMONG ELECTRIC SPARKS, LASER-INDUCED PLASMAS AND UV LIGHT

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C.P. McKay, W. J. Borucki, L.P. Giver, H. Van Ghyseghem
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The chemistry in planetary atmospheres that is induced by processes associated with high-temperature plasmas is of broad interest because such processes may explain many of the chemical species observed. There are at least two important phenomena that are known to generate plasmas (and shocks) in planetary atmospheres: lightning and meteor impacts. Lightning has long been recognized to be an important driver of chemical reactions in the Earth's atmosphere and, probably, in the atmospheres of Jupiter, Saturn and Venus. Lightning may also have provided a source for prebiotic compounds on the early Earth. Meteors and cometary objects impacting planetary atmospheres may have supplied prebiotic compounds to or initiated chemical processes in the atmospheres. For both lightning and impacts, rapid heating of atmospheric gases leads to the formation of a high-temperature plasma which emits radiation and produces shock waves that propagate through the surrounding atmosphere. These processes initiate chemical reactions that can transform simple gases into more complex compounds. For example, electric discharges in mixtures of $H_2/CH_4/NH_3$ and CH_4/N_2, representing the atmospheres of Jupiter and Titan, respectively, are known to produce a suite of gaseous and condensed phase hydrocarbons and C-N containing compounds. Also, processing of Titan's early atmosphere from impacts of meteors and comets may have been responsible for the molecular nitrogen still there today.

In order to study the production of organic compounds in plasmas (and shocks), various mixtures of N_2, CH_4, and H_2, modeling the atmosphere of Titan, were exposed to discrete sparks, laser-induced plasmas (LIP) and ultraviolet light. The yields of HCN and simple hydrocarbons were measured and compared to those calculated from a simple quenched thermodynamic equilibrium model. The agreement between experiment and theory was fair for HCN and C_2H_2. However, the yields of C_2H_6 and other hydrocarbons were much higher than those predicted by the model. Our experiments suggest that photolysis by ultraviolet light from the plasma is an important process in the synthesis. This was confirmed by the photolysis of gas samples exposed to the light, but not to the plasma or shock waves. The results of these experiments demonstrate that , in addition to the well-known efficient synthesis of organic compounds in plasmas, the yields of saturated species, e.g. ethane, may be higher than predicted by theory and that LIP provide a convenient and clean way of simulating planetary lightning and impact plasmas in the laboratory.

ORGANIC SYNTHESIS IN THE OUTER SOLAR SYSTEM: RECENT LABORATORY SIMULATIONS FOR TITAN, THE JOVIAN PLANETS,TRITON AND COMETS

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The atmosphere of Titan is composed mainly of N_2, with 3-12% CH_4 (depending on altitude and details of the surface equilibrium). Voyager revealed Titan to be covered by a thick haze; the optical properties of this haze derived by scattering models are consistent with those of organic heteropolymer (tholin) produced in the laboratory by a plasma discharge in 90% N_2-10% CH_4. Abundant amino acids are produced from this tholin on hydrolysis . We have recently analyzed the volatile products of continuous flow plasma excitation of this atmosphere (generated on Titan primarily by Saturnian magnetospheric electrons and solar and galactic cosmic rays), and find some 60 products, including many multiply-bonded hydrocarbons and nitriles.

We tabulate below the most abundant gases and their radiation yields, for two experimental pressures: 0.24 mb, more relevant to upper atmosphere excitation, and 17 mb, more relevant to tropospheric, cosmic ray excitation. The yields computed in the 0.24 mb experiment combined with measured electronic fluxes and a simple, eddy diffusion model of Titan's atmosphere predict abundances of detected molecules in agreement with those found by Voyager and for heavier products, in somewhat better agreement with observation than photochemical absolute reaction rate kinetics models . All Voyager organics are accounted for and no detectable products are found that Voyager did not detect. A striking increase of products with multiple bonds is found with decreasing pressure. Hydrocarbon abundances decline slowly with increasing carbon number.

Additionally, we list preliminary estimates for the yield of the heteropolymer, which seems to be produced in a quantity comparable (in moles of C+N consumed) to the total amount of gaseous product. The production rate required to sustain Titan's haze against sedimentation also indicates yields of this order . As can be seen from the table, over 10^9 years substantial amounts of these products can accumulate on the surface -- ranging from cm thicknesses for the (C+N=4) species to a meter or more for HCN and C_2H_2; we also expect a meter or more of tholins.

Similar analyses have been or are being done for the Jovian planets and Triton.

Charged particle irradiation of hydrocarbon clathrates or mixed hydrocarbon/water ices produces a range of organic products, reddening and darkening of the ices and characteristic infrared spectra. From such spectra, the predicted emission by fine particles in cometary comae well-matches the observed 3.4 μm emission spectra of Comet Halley and other recent comets. Heliocentric evolution of organic emission features in comets is predicted. Organic products of such ice irradiation may account for colors and albedos on some of the satellites in the outer solar system, especially Triton and Pluto, where solid methane is known to exist.

Titan Continuous Flow Simulation Results
(from W.R. Thompson, T. Henry, J. Schwarts, B.N. Khare, and C. Sagan, *Icarus*, in press)

Species	G, 17 mb molec/100 eV	G, 0.24 mb molec/100 eV	Voyager IRIS	Kinetic Chemical Model$^+$	This Work$^+$	Column Density gm/cm^2/10^9 y
$HC\equiv CH$	1.6×10^{-1}	3.9×10^{-3}	2×10^{-6}	4.0×10^{-6}	$0.3\text{-}1.3 \times 10^{-6}$	150 - 1770
$HC\equiv N$	3.3×10^{-2}	1.6×10^{-1}	2×10^{-7}	5.6×10^{-7}	$1.8\text{-}9.0 \times 10^{-7}$	50 - 330
$N\equiv C\text{-}C\equiv N$	3.6×10^{-3}	2.8×10^{-3}	10^{-7} - 10^{-8}	1.9×10^{-8}	$1.4\text{-}7.0 \times 10^{-8}$	7.3 - 28
$HC\equiv C\text{-}C\equiv N$	2.4×10^{-3}	8.8×10^{-3}	10^{-7} - 10^{-8}	5.6×10^{-8}	$1.6\text{-}8.0 \times 10^{-8}$	6.1 - 51
$CH_3C\equiv N$	1.5×10^{-3}	4.6×10^{-3}	-----	-----	$0.7\text{-}3.2 \times 10^{-8}$	2.8
$CH_3\text{-}C\equiv CH$	1.4×10^{-3}	1.9×10^{-2}	3×10^{-8}	1.8×10^{-7}	$0.3\text{-}1.4 \times 10^{-8}$	5 - 130
$H_2C{=}CH\text{-}CH{=}CH_2$	1.3×10^{-3}	1.7×10^{-3}	-----	-----	$0.6\text{-}3.0 \times 10^{-8}$	2.8
$HC\equiv C\text{-}C\equiv CH$	8.2×10^{-4}	1.5×10^{-3}	10^{-7} - 10^{-8}	7.8×10^{-10}	$0.4\text{-}1.8 \times 10^{-8}$	1.7
$H_2C{=}C{=}CH_2$	7.7×10^{-4}	1.6×10^{-2}	-----	-----	$1.5\text{-}7.5 \times 10^{-9}$	3.8
$H_2C{=}CH\text{-}C\equiv CH$	2.4×10^{-4}	1.7×10^{-3}	-----	-----	$1.1\text{-}5.5 \times 10^{-9}$	0.8
$H_2C{=}CH\text{-}C\equiv N$	1.9×10^{-4}	1.3×10^{-3}	-----	-----	$0.8\text{-}4.1 \times 10^{-9}$	0.6
Heteropolymers*	- 0.2-2	- 0.2-2				100 - 1000

*Units of measure are total atoms (C+N). $^+$These volume mixing ratios derive from simple eddy diffusion models of vertical transport. Laboratory results are shown for 0.24 mb, roughly where magnetospheric electrons drive atmospheric chemistry.

PHOTOCHEMICAL REACTIONS OF CYANOACETYLENE AND DICYANOACETYLENE: POSSIBLE PROCESSES IN TITAN'S ATMOSPHERE

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Titan has an atmosphere which is subject to dramatic chemical evolution due mainly to the dramatic effect of the UV flux from the Sun. The energetic solar photons and other particles are converting the methane-nitrogen atmosphere into the unsaturated carbon compounds observed by the Voyager probes. These same solar photons are also converting some of these unsaturated reaction products into the aerosols observed in the atmosphere which obscure the view of the surface of Titan. In particular, the photochemical reactions of cyanoacetylene, dicyanoacetylene, acetylene and ethylene may result in the formation of the higher hydrocarbons and polymers which result in the aerosols observed in Titan's atmosphere.

Polymers are the principal reaction products formed by irradiation of cyanoacetylene and dicyanoacetylene. Irradiation of cyanoacetylene with 185 nm of light also yields 1,3,5-tricyanobenzene while irradiation at 254 nm yields 1,2,4-tricyanobenzene and tetracyanocyclooctatetraenes. Photolyses of mixtures of cyanoacetylene and acetylene yields mono- and di- cyanobenzenes. 1-Cyanocyclobutene is formed from the photochemical addition of cyanoacetylene with ethylene. The photolysis of dicyanoacetylene with acetylene yields 2,3-dicyano-1,3-butadiene and 1,2-dicyanobenzene. Tetracyanocyclooctatetraene products were also observed in the photolysis of mixtures of dicyanoacetylene and acetylene with 254 nm light. 1,2-Dicyanocyclobutene is obtained from the photolysis of dicyanoacetylene and ethylene. Reaction mechanisms will be proposed to explain the observed photoproducts.

CONTROLLED EVOLUTION OF AN RNA ENZYME

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It is generally thought that prior to the origin of protein synthesis, life on earth was based on self-replicating RNA molecules. This idea has become especially popular recently due to the discovery of catalytic RNA (ribozymes). RNA has both genotypic and phenotypic properties, suggesting that it is capable of undergoing Darwinian evolution. RNA evolution is likely to have played a critical role in the early history of life on earth, and thus is important in considering the possibility of life elsewhere in the solar system. We have constructed an RNA-based evolving system in the laboratory, combining amplification and mutation of an RNA genotype with selection of a corresponding RNA phenotype. This system serves as a functional model of a primitive organism. It can also be used as a tool to explore the catalytic potential of RNA. By altering the selection constraints, we are attempting to modify the substrate specificity of an existing ribozyme in order to develop ribozymes with novel catalytic function. In this way, we hope to gain a better understanding of RNA's catalytic versatility and to assess its suitability for the role of primordial catalyst.

All of the RNA enzymes that are known to exist in contemporary biology carry out cleavage/ligation reactions involving RNA substrates. The *Tetrahymena* ribozyme, for example, catalyzes phosphoester transfer between a guanosine-containing and an oligopyrimidine-containing substrate. We tested the ability of mutant forms of the *Tetrahymena* ribozyme to carry out a comparable reaction using a DNA, rather than RNA substrate. An ensemble of structural variants of the ribozyme was prepared and tested for their ability to specifically cleave d(GGCCCTCT•A_3TA_3TA) at the phosphodiester bond following the sequence CCCTCT. We recovered a mutant form of the enzyme that cleaves DNA more efficiently than does the wild-type. Beginning with this selected mutant we have now scattered random mutations throughout the ribozyme and have begun an evolutionary search to further expand the catalytic repertoire of RNA.

SOURCES AND GEOCHEMICAL EVOLUTION OF CYANIDE AND FORMALDEHYDE

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Although several systems have been proposed to be capable of molecular recognition and replication, only purine-pyrimidine base pairing has been experimentally demonstrated to perform those combined functions. Early precursors of RNA may be assumed to have utilized a minimum of two nitrogen bases attached to acyclic hydroxyaldehydes, and originally, or at a more advanced stage, to have incorporated phosphate linkages. Such an evolution would require satisfactory sources of cyanide, simple aldehydes, and reactive phosphate species. Furthermore, efficient geochemical mechanisms are needed to selectively concentrate these components into an environment where appropriate reactions can be demonstrated to be possible and probable.

The major source of cyanide has, in current paleoatmospheric models, been assumed to be the reaction of photodissociated thermospheric nitrogen with a limiting supply of stratospheric methane. Formaldehyde may be produced with more ease from an atmosphere with an atmosphere of carbon dioxide as the dominant carbon species, and from carbonate in solution or sorbed in double-layer hydroxide minerals.

Potentially more important sources for cyanide and other carbon containing molecules are the partially photoprotected northern and southern auroral ovals where continuous currents reaching several mega-amperes induce ion-molecule reactions, extending into the lower stratosphere - in simulated environments of this kind cyanide ion is known to be produced from oxidized carbon species potentially more abundant than methane.

Rainout of cyanide and formaldehyde place them in two different geochemical reaction reservoirs. In the anoxic Archean hydrosphere, about 1 mM in Fe^{2+}, cyanide ion would have been efficiently converted to the stable ferrocyanide complex $Fe(CN)_6^{4-}$, protecting it from the commonly considered fate of decomposition by hydrolysis, and eventually incorporating it in pyroaurite materials type minerals, most efficiently in green rust where it converts to insoluble ferriferrocyanide, prussian blue.

In snow and firn the Sanchez-Orgel freezeout process would lead to eutectic concentration of glycolonitrile and its oligomers as reaction products of cyanide and formaldehyde, the latter probably always present in excess.

The cyanide in the hydrosphere, strongly bound to ferrous iron, is shown experimentally to be liberated on photooxidation of ferrocyanide with concurrent precipitation of γ-FeOOH. In the presence of an equimolar or larger fraction of formaldehyde in 10mM solution pH 7, the liberated cyanide practically completely converts to glycolonitrile.

The seemingly ubiquitous cyanohydrin production inferred from the Archean cryosphere and hydrosphere focuses the attention on the following evolution of these compounds. Glycolonitrile (formaldehyde cyanohydrin) in neutral or weakly alkaline solution oligomerizes along two different paths. One, kinetically favored at low temperatures, such as in the Sanchez-Orgel situation, leads to a crystallizable compound, presumed to be 6-amino-5-hydroxy-2,4-pyrimidine dimethanol. The prospect of spontaneous formation of such a pyrimidine from geochemically plausible source is of interest for biopoesis; the structure and reactivity of this model is now being investigated.

The second reaction of glycolonitrile, kinetically dominant at ambient temperature, produces a light yellow oligomer, which at increasing polymerization turns into a brown, viscous liquid and eventually to a black solid. Hydrolysis and pyrolysis of such a polymer may provide a source of amino compounds and ammonia, difficult to produce and maintain in the Archean atmosphere.

KAOLINITE-CATALYZED AIR OXIDATION OF HYDRAZINE: CONSIDERATION OF SEVERAL COMPOSITIONAL, STRUCTURAL AND ENERGETIC FACTORS IN SURFACE ACTIVATION

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It appears from the fossil record that single-celled terrestrial life forms had proliferated by 0.7-0.9 b.y. after the formation of the earth. Since impact heating did not end until several hundred million years after the bulk accretion, a very narrow window has been established for the complex sequence of precursive chemical processes required to produce, collect and assemble the organic constituents of cellular life. It has long been recognized by biologists that surfaces, particularly those with special sites, i.e. phospholipid membranes with protein receptors and channels, have unique and varied functional properties, including the capacity to differentially recognize and act to alter or transport materials. It has been even longer accepted by chemists that solid surfaces have powerful catalytic properties that cannot be even approximately explained by their bulk chemical composition and structure. By contrast, the Origin of Life Community has been dishearteningly grudging in its acceptance even of the concept (much less the need for careful investigation) of the fact that terrestrially abundant mineral surfaces, particularly those with structural defects, have powerful informational and energetic properties. Natural surfaces show not only a potential, but a capacity to promote chemical reactions leading to the synthesis and oligomerization of biologically significant monomers under conditions that better represent those of early earth than do single phase models. Homogeneous, single-phase, artificial laboratory models for organic synthesis of biologically significant molecules still 'rain' supreme from the atmosphere to the soup. Leading scholars of organic material in comets and interstellar ices still pass off mineral grains as "inert silicaeous contaminants" with a straight face in the O. of L. and Space Sciences Communities with scholarly and funding impunity. For some minerals, their complexity is adequate to sustain membrane, even whole cell, molecular operations of types required to emulate the functional attributes of living systems. It can be postulated that the specific adsorption and catalytic powers of these special minerals may prove adequate to adequate to produce a translation mechanism between inorganic protolife systems and self-organizing assemblies of organic molecules capable of serving as organic protolife forms.

Clay minerals have been shown to have numerous,curious, energetic properties by virtue of ultra-violet light release which can be triggered by gentle environmental changes such as wetting and dewetting by a variety of liquids, unique among them water and hydrazine. Since both water and hydrazine play multiple key roles in the air-oxidation of hydrazine on kaolinite surfaces, this reaction would seem to have prime potential for studying interrelationships of energy storage, release and chemical reactivity of clay surfaces, capacities basic to either the Bernal or Cairns-Smith roles of minerals in the origin of life. Establishment of the capacity for stored electronic energy to significantly alter surface chemistry is important, regardless of the reaction chosen to demonstrate it. Hydrazine air oxidation is overawingly complex, given the possibilities for step-wise control and monitoring of parameters. In the light of recently extended characterization of the kaolinite and model sheet catalysts we used to study hydrazine oxidation, gamma-irradiated silica, previous studies of hydrazine air-oxidation on aluminosilicate surfaces have been reevaluated. Our former conclusion remains intact that, whereas trace structural and surface contaminants do play some role in the catalysis of oxidation, they are not the only, nor even the dominant, catalytic centers. Initial intermediates in the oxidation can now be proposed which are consistent with production via O^--centers as well as ferric iron centers. The greater than square dependence of the initial reaction rate on the weight of the clay is discussed in the light of these various mechanistic possibilities.

TERRESTRIAL PRODUCTION VS. EXTRATERRESTRIAL DELIVERY OF PREBIOTIC ORGANICS TO THE EARLY EARTH

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Since early in this century, it has been speculated that Earth may have accreted much of the prebiotic organics necessary for the origins of life from impacts of carbonaceous asteroids or comets. This accretion would have been greatest during the period of heavy bombardment 4.5 to 3.8 Gyr ago. Over the last decade, this potential extraterrestrial source of organic molecules for the primitive Earth has taken on new importance, as an emerging consensus in planetary science has replaced previous models of a primordial reducing (CH_4/NH_3-rich) terrestrial atmosphere with that of a neutral (CO_2/N_2) one. Synthesis of key prebiotic molecules in CO_2 atmospheres has been shown experimentally to be much more difficult than in reducing ones, with production efficiencies dropping precipitously by many orders of magnitude as the ration H_2/CO_2 falls below unity. However, while these results are suggestive, there is certainly at present no requirement to invoke exogenous organics to account for the evolution of life on Earth. Many other speculative mechanisms for terrestrial prebiotic synthesis have been suggested. The goal of investigators at present must be to quantify as best as possible prebiotic organic production from the various proposed sources, so that their comparative importance may be weighed. A kind of "balance sheet" for organic production from different sources in various putative early terrestrial atmospheres may then be constructed.

A comprehensive treatment of comet/asteroid interaction with the atmosphere, ensuring surface impact, and resulting organic pyrolysis is required to determine whether more than a negligible fraction of the organics in incident comets and asteroids actually survived collision with Earth. Results of such an investigation, using a smoothed particle hydrodynamic simulation of cometary and asteroidal impacts into both oceans and rock, demonstrate that organics will not survive impacts at velocities $\gtrsim 10$ km s^{-1}, and that even comets and asteroids as small as 100m in radius cannot be aerobraked to below this velocity in 1 bar atmospheres. However, for plausible dense (10 bar CO_2) early atmospheres, there will be sufficient aerobraking during atmospheric passage for some organics to survive the ensuing impact. Combining these results with analytical fits to the lunar impact record shows that 4.5 Gyr ago Earth was accreting at least $\sim 10^6$ kg yr^{-1} of intact cometary organics, a flux which thereafter declined with a ~100 Myr half-life. The extent to which this influx was augmented by asteroid impacts, as well as the effect of more careful modelling of a variety of conservative approximations, is currently being quantified. These results may be placed in context by comparison with *in situ* organic production from a variety of terrestrial energy sources, as well as organic delivery by interplanetary dust. Which source dominated the early terrestrial prebiotic inventory is found to depend on the nature of the early terrestrial atmosphere. However, there is an intriguing symmetry: It is exactly those dense CO_2 atmospheres where *in situ* atmospheric production of organic molecules should be the most difficult, in which intact cometary organics would be delivered in large amounts.

SELF ASSEMBLY PROPERTIES OF PRIMITIVE ORGANIC COMPOUNDS

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A central event in the origin of life was the self-assembly of amphiphilic, lipid-like compounds into closed microenvironments. If a primitive macromolecular replicating system could be encapsulated within a vesicular membrane, the components of the system would share the same microenvironment, and the result would be a step toward true cellular function. The goal of our research has been to determine what amphiphilic molecules might plausibly have been available on the early Earth to participate in the formation of such boundary structures. To this end, we have investigated primitive organic mixtures present in carbonaceous meteorites such as the Murchison meteorite, which contains 1-2 percent of its mass in the form of organic carbon compounds. It is likely that such compounds contributed to the inventory of organic carbon on the prebiotic earth, and were available to participate in chemical evolution leading to the emergence of the first cellular life forms.

We found that Murchison components extracted into non-polar solvent systems are surface active, a clear indication of amphiphilic character (Deamer and Pashley, Origins of Life and Evolution of the Biosphere 19 (1989) 21-33.) One acidic fraction self-assembles into vesicular membranes that provide permeability barriers to polar solutes. Other evidence indicates that the membranes are bimolecular layers similar to those formed by contemporary membrane lipids. We conclude that bilayer membrane formation by primitive amphiphiles on the early Earth is feasible. However, only a minor fraction of acidic amphiphiles assembles into bilayers, and the resulting membranes require narrowly defined conditions of pH and ionic composition to be stable. It seems unlikely, therefore, that meteoritic infall was a direct source of membrane amphiphiles. Instead, the hydrocarbon components and their derivatives more probably would provide an organic stock available for chemical evolution. Our current research is directed at possible reactions which would generate substantial quantities of membranogenic amphiphiles. One possibility is photochemical oxidation of hydrocarbons. For instance, we have found that pyrene, a major polycyclic aromatic hydrocarbon of carbonaceous meteorites, acts as a photosensitizer in the hydroxylation of long chain hydrocarbons. This reaction is significant, in that a non-polar species (the hexadecane) becomes a surface-active molecule which would be available to partake in membrane formation.

STRUCTURE AND FUNCTIONS OF WATER-MEMBRANE INTERFACES AND THEIR ROLE IN PROTO-BIOLOGICAL EVOLUTION

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Among the most important developments in proto-biological evolution was the emergence of membrane-like structures. These are formed by spontaneous association of relatively simple amphiphilc molecules that would have been readily available in the primordial environment. The resulting interfacial regions between water and nonpolar interior of the membrane have several properties which made them uniquely suitable for promoting subsequent evolution. They can a) selectively attract organic material and mediate its transport, b) serve as simple catalysts for chemical reactions, and c) promote the formation of trans-membrane electrical and chemical gradients which could provide energy sources for proto-cells. Understanding the structure of interfaces, their interactions with organic molecules and molecular mechanisms of their functions is an essential step to understanding proto-biological evolution.

In our computer simulation studies, we showed that the structure of water at interfaces with nonpolar media is significantly different from that in the bulk. In particular, the average surface dipole density points from the vapor to the liquid. As a result, negative ions can approach the interface more easily than positive ions. Amphiphilic molecules composed of hydrocarbon conjugated rings and polar substituents (e.g., phenol) assume at the interface rigid orientations in which polar groups are buried in water while hydrocarbon parts are located in the nonpolar environment. These orientational differences are of special interest in connection with the ability of some of these molecules to efficiently absorb photons. Flexible molecules with polar substituents often adopt at interfaces conformations different from those in the bulk aquaeous solution and in the gas phase. As a result, in many instances both specificity and kinetics of chemical reactions in which these molecules can participate is modified by the presence of surfaces.

Of special interest is the mechanism by which polar molecules are transferred across interface between water and a nonpolar medium. Our recent study showed that simple ionophores bind ions by the same mechanisms as ion channels and carriers from modern cells. In particular, upon binding the ion these ionophores undergo change in which their polar groups come into close contact with the ion and get buried in the interior of the carrier. Simultaneously, groups soluble in oil become exposed to the surface allowing the complex to penetrate the oily environment of the membrane. Thus, our study lends support to one of the main concepts in studies of biochemical evolution: that physico-chemical mechanisms of ubiquitous cell functions remained similar throughout evolution, but became more accurate and efficient as the molecules performing these functions gained structural complexity.

MACROMOLECULAR RECOGNITION: STRUCTURAL ASPECTS OF THE ORIGIN OF THE GENETIC SYSTEM

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Theoretical simulation of prebiotic chemical processes is an invaluable tool for probing the phenomenon of evolution of life. Using computational and modeling techniques and guided by analogies from present day systems we seek to understand the emergence of genetic apparatus, enzymatic catalysis and protein synthesis under prebiotic conditions. In one possible scenario, the RNA enzymatic reaction plays a key role in the emergence of the self-replicating and offers a clue to the onset of enzymatic catalysis prior to the existence of the protein biosynthetic machinery. Our ultimate goal is to propose a simple RNA segment which contains the specificity and catalytic activity of the contemporary RNA enzyme and which could emerge in a primordial chemical environment. To understand the mechanism of ribozyme catalyzed reactions ab *initio* and semi-empirical (ZINDO) programs were used to investigate the reaction path of transphosphorylation, A special emphasis was placed on the possible catalytic and structural roles played by the coordinated magnesium cation. Both the inline and adjacent mechanisms of transphosphorylation have been studied. Another important aspect of this reaction is the identity of the functional groups which are essential for the acid base catalysis. The structural characteristics of the target helices, particularly a possible role of G•T pair, is under examination by molecular dynamics (MD) simulation technique.

Modeling of the ancestral aminoacyl-tRNA-synthetases (aRS) may provide important clues to the emergence of the genetic code and the protein synthetic machinery. Assuming that the catalytic function evolved before the elements of specific recognition of a particular amino acid we are exploring the minimal structural requirements for the catalysis of tRNA aminoacylation. The molecular modeling system SYBYL was used for this study based on the high resolution crystallographic structures of the present day tyrosyl-adenylate:tyrRS and $\mathrm{tRNA^{Gln}}$: ATP:glnRS complexes. The trinucleotide CCA of the 3'-end tRNA is placed into the active site pocket of tyrRS, based on the scheme of interaction between $\mathrm{tRNA^{Gln}}$ and glnRS, and upon the stereochemistry of the tyrRS:tRNA:Tyr-AMP transition state. This provides a model of the non-specific recognition of a tRNA's 3'-end by an aRS, which might be similar to that of the ancestral aRS's. In the next step modeling of the interaction of the rest of the acceptor stem of $\mathrm{tRNA^{Tyr}}$ with tyrRS is carried out.

TEMPLATE POLYMERIZATION OF NUCLEOTIDE ANALOGUES

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Recent work on the template-directed reactions of the natural D-nucleotides has made it clear that L-nucleotides and nucleotide-like derivatives of other sugars would strongly inhibit the formation of long oligonucleotides. Consequently, attention is focusing on molecules simpler than nucleotide that might have acted as the monomers of an information-transfer system. We have begun a general exploration of the template-directed reactions of diverse peptide analogues.

I will present work by Dr. Kazuo Harada showing analogues in which phosphate groups are replaced by carboxylate groups will undergo template-directed oligomerization provided cyclization is prevented. I will also present work by Dr. Taifeng Wu on oxidative oligomerization of phosphorothioates and of Dr. Mary Tohidi on the cyclic polymerization of nucleoside and related cyclic pyrophosphates.

PRODUCT AND RATE DETERMINATIONS WITH CHEMICALLY ACTIVATED NUCLEOTIDES IN THE PRESENCE OF VARIOUS PREBIOTIC MATERIALS, INCLUDING OTHER MONO- AND POLYNUCLEOTIDES

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Template-directed syntheses of polynucleotides in the absence of enzymes provide a promising model for the evolution of replicating systems and the concurrent transfer of information from one generation to the next. In today's enzymatic systems, polynucleotide synthesis uses the triphosphate mononucleotides as building blocks. Although these molecules are chemically activated and serve as the energy source in most biological syntheses, they exhibit a large barrier to non-enzymatic reaction. Hence, in order to compensate for the large reductions in rates that occur when no enzyme catalysts are present, modeling experiments are performed with similarly activated but chemically more labile monomeric precursors. Indeed, phosphoimidazolide activated nucleotides, so called ImpN's, have found widespread application in template-directed chemistry.

The most interesting reaction of ImpN's is the template-directed oligomerization in the presence of the appropriate template. However, the efficiency of this reaction depends dramatically on the competition with other reactions that consume ImpN's. Therefore we are investigating the reactions of ImpN's in the presence of a number of prebiotically plausible materials, such as metal ions, phosphate, amines and other nucleotides and hope to learn more about the stability/reactivity of ImpN's in a prebiotic aqueous environment. Although ImpN's hydrolyze readily, we find that, in the presence of phosphate, ImpN form substantial amounts of diphosphate nucleotides. These diphosphate nucleotides are not very good substrates for template-directed reactions, but are chemically activated and are known to revert to the phosphoimidazolides in the presence of imidazole under solid-state conditions. With respect to our studies of the oligomerization reaction, the determination of the dimerization rate constant of a specific ImpN (guanosine 5'-phospho-2-methylimidazolide) both in the absence and in the presence of the template lead to the conclusion that at 37°C the dimerization is not template-directed although the subsequent polymerization steps are. In other words this specific polynucleotide synthesizing system favors the elongation of oligonucleotides as compared with the formation of dimers and trimers. This favoring of the synthesis of long as opposed to short oligonucleotides may be regarded as a rudimentary example of natural selection at the molecular level.

CARBOHYDRATES AS A SOURCE OF ENERGY AND MATTER FOR THE ORIGIN OF LIFE

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One of the most important questions concerning the origin of life is the nature of the primitive process that provided the chemical energy necessary for the emergence of biological complexity. We have approached this question by studying chemical reactions that resemble glycolysis in the way they yield useful chemical energy. The central role of glycolysis in metabolism plus its ability to function under the anaerobic conditions of early Earth suggest that it may have provided the energy needed for the origin of life. Our chemical studies have focused on the first energy-yielding step of glycolysis involving the oxidation of glyceraldehyde-3-P which initially yields an 'energy-rich' glyceroyl enzyme thioester that drives the synthesis of ATP via a 1,3-diphosphoglycerate intermediate. Our previous nonenzymatic studies established that glyceraldehyde oxidation in the presence of a thiol yields 'energy-rich' thioesters and that thioesters can act as condensing agents for the synthesis of phosphoanhydrides.

Recently, we proposed a new model of early glycolysis in which the oxidation of glyceraldehyde self-hemiacetals yielded 'energy-rich' polyglyceric acid instead of 'energy-rich' thioesters. In this model, polyglyceric acid not only acts as an energy source for phosphoanhydride synthesis, but also as an autocatalyst that can replicate the sequence of D- and L-residues in its structure. We began our investigation of this new hypothesis - the triose model - by developing a thermal method for the racemization-free synthesis of polyglyceric acid. The hydrolytic stability and the role of chirality in interactions of polyglyceric acid were studied using this thermal polymer. Next, we established that the the 2- and 3-glycerol esters of polyglyceric acid are 'energy-rich' by measuring the Gibbs free energy change of hydrolysis ($\Delta G^{\circ\prime}$, pH 7) of the 2- and 3-glycerol esters of 2- and 3-O-L glyceroyl-glyceric acid methyl ester -- a model of polyglyceric acid. The ΔG° of 2- and 3-glycerol esters were -9.1 kcal/mol and -7.8 kcal/mol, respectively. Recently, we discovered 1) that glyceraldehyde is bound and oxidized to glyceric acid on the surface of ferric hydroxide, and 2) that soluble ferric ion catalyzes the rearrangement of glyceraldehyde to lactic acid. We are exploring the possibility that these reactions could yield polyglyceric acid and polylactic acid under plausible prebiotic conditions.

ON THE ORIGIN AND EARLY EVOLUTION OF BIOLOGICAL CATALYSIS AND OTHER STUDIES ON CHEMICAL EVOLUTION

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One of the lines of research in molecular evolution which we have developed for the past three years is related to the experimental and theoretical study of the origin and early evolution of biological catalysis. In an attempt to understand the nature of the first peptidic catalysts and coenzymes, we have achieved the non-enzymatic synthesis of the coenzymes ADPG, GDPG, and CDP-ethanolamine, under conditions considered to have been prevalent on the primitive Earth. We have also accomplished the prebiotic synthesis of histidine, as well as histidyl-histidine, and we have measured the enhancing effects of this catalytic dipeptide on the dephosphorylation of deoxyribonucleotide monophosphates, the hydrolysis of oligo A, and the oligomerization 2',3' cAMP.

On the theoretical side, we have reviewed and further developed the hypothesis that RNA preceded double-stranded DNA molecules as a reservoir of cellular genetic information. This has led us to undertake the study of extant RNA polymerases in an attempt to discover vestigial sequences preserved from early Archean times. So far, we have been able to develop an evolutionary classification of all extant cellular and viral RNA polymerases into a few families both on the basis of the amino acid sequences and function. Moreover, since the "RNA prior to DNA hypothesis" implies that reverse transcription is a very old phenomenon dating from the Archean Eon, we have analyzed the substrate specificities of several retroviral reverse transcriptases (including that of the AIDS virus) and discovered that under slightly modified laboratory conditions, these RNA dependent DNA polymerases behave as replicases, that is, as RNA dependent RNA polymerases.

In addition to the above research we have also continued our studies on the chemical evolution of organic compounds in the solar system and beyond. Hydrogenolysis by means of deuterium chloride of iron and other metal carbides found in meteorites has demonstrated the formation of aliphatic hydrocarbons from C_1 to C_7, an experimental finding which is in line with the recent observations of homonuclear linear carbon species in circumstellar clouds.

We have also suggested a simple mechanism for the high enrichment of deuterium found by other investigators in the amino acids of the Murchison meteorite, and we have developed arguments for the presence of anaerobic life in Europa in light of recent discussions about the possibility of a subsurface ocean in this satellite. These different lines of research in chemical evolution and exobiology have been carried out with the collaboration of G. Armangue, G. Fox, A. Mar, C. Marquez, T. Mills, and C. Shen.

CHEMISTRY OF AMINOACYLATION OF 5'-AMP AND THE ORIGIN OF PROTEIN SYNTHESIS

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For many years our work centered around understanding the molecular basis for the origin of the genetic code. As that work progressed, it became more and more obvious that in order to understand the origin of coding, we needed to understand the origin of the process of protein synthesis. So, our work in the last few years has shifted to the study of chemical reactions and interactions related to the process of protein synthesis.

In contemporary protein synthesis, each amino acid is first activated by ATP and becomes an aminoacyl adenylate anhydride. From that compound, it is passed to become a 2' (3') ester of the 3' terminal 5'-AMP residue of tRNA. A new peptide bond is then formed between that amino acid ester and the growing peptide on an adjacent tRNA.

The chemistry of protein synthesis is thus the chemistry of aminoacyl AMP. Consequently much of our recent work has been a study of aminoacyl AMP derivatives. Elucidation of the character of aminoacyl AMP reactions has made it obvious that AMP (and perhaps other purine monoribonucleotides) has characteristics which should allow it to preferentially catalyze the synthesis of L-amino acid peptides. The essential features which lead to this conclusion are: (1) all L-amino acids (but not all D amino acids) when esterified to 5'-AMP preferentially (65%) distribute to the 3' position of the 5'-AMP. (2) esterification is predominantly at the 2' position. (3) 2', 3' diaminoacyl esters are readily formed. (4) a peptide bond can be formed between adjacent 2', 3' aminoacyl esters.

The experimental data concerning these characteristics of 5'-AMP will be presented with discussion of how they may have served to direct the origin and evolution of protein synthesis, including the use of L-amino acids.

CATALYTIC RNA AND SYNTHESIS OF THE PEPTIDE BOND

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The existence of catalytic RNA has suggested to some workers that in the earliest organisms RNA could have been both genetic material and catalyst. Although there are problems with current theories of how these organisms may have arisen, it is possible that translation was a relatively late invention by RNA organisms that already had evolved a considerable degree of biochemical complexity[1]. The range of reactions that RNA is known to catalyze is limited, but it is possible that it once may have carried a greater variety of functional groups, and therefore may have been able to catalyze a greater variety of reactions. In collaboration with Tom Cech and Mike Yarus at the University of Colorado, Boulder, we are studying whether the L-19 IVS ribozyme from *Tetrahymena thermophila* can catalyze the formation of the peptide bond when it is supplied with synthetic aminoacyl oligonucleotides. If this reaction works, it could give us some insight into the mechanism of peptide bond formation and the origin or coded protein biosynthesis.

Two short oligoribonucleotides, CCCCC and a protected form of CCCCU were prepared; the former was made by the controlled hydrolysis of poly(C), and the latter by multistep chemical synthesis from the protected monomers. The homopentamer was then aminoacylated using ^{14}C-labelled Boc-protected glycine imidazolide. This aminoacylated oligo-nucleotide has now been shown to enter the active site of the L-19 IVS, and aminoacyl transfer and peptide bond formation reactions are being sought. Our synthesis of CCCCU made us aware of the inadequacy of many of the 2'-hydroxyl protecting groups that are in use today and we therefore designed a new 2'-protecting group that is presently being tested.

1. S. A. Benner and A. D. Ellington, *Nature*, **329**, 295-6 (1987).

NEW EVIDENCE FOR A DRAMATIC RISE IN ATMOSPHERE OXYGEN CA. 1,900 M.Y. AGO

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The evolution of the oxygen content of the Earth's atmosphere has been tied closely to the history of the biosphere. Before the advent of life, the O_2 content of the atmosphere must have been vanishingly small. At the beginning of the Phanerozoic, ca. 570 m.y. ago, P_{O_2} must have been at least 10% of the present O_2 level of o.2 atm. During the past 300 m.y. P_{O_2} was almost certainly more than half and less than twice the present level. To date, the O_2 content of the atmosphere between the origin and life and the opening of the Phanerozoic has been very poorly constrained. Several lines of geologic evidence have pointed to a significant increase in P_{O_2} about 2,000 m.y. ago, but the magnitude of P_{O_2} before and after that time has been quite uncertain. The data that we have accumulated recently suggest that P_{O_2} was $\leq 2 \times 10^{-3}$ atm more than 2,000 m.y. ago, and ≥ 0.03 atm more recently than ca. 1,900 m.y. ago.

These estimates are based on the behavior of iron in Precambrian weathering horizons. More than ca. 2,000 m.y. ago Fe^{+2} released during the weathering of basalts was not oxidized to Fe^{+3}, and was removed in ground water from the upper layers of soil horizons. More recently than ca. 1, 850 m.y. ago, Fe^{+2} was oxidized to Fe^{+3} and precipitated as iron oxides and hydroxides in such soil horizons and in the weathering products of a carbonate facies banded iron formation in Griqualand West, South Africa. The O_2 content of the atmosphere must have increased dramatically about 1,900 m.y. ago to explain these observations. The reasons for the increase are still obscure, but are probably related to changes in the biologic productivity of the oceans. Eukaryotes appear to have developed shortly after the increase in P_{O_2}, perhaps in response to the subsequent increase in the supply of nitrate from the atmosphere to the oceans.

BIOSPHERIC-ATMOSPHERIC COUPLING ON THE EARLY EARTH

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Over the history of our planet, the production of gases within the biosphere and their release into the atmosphere have had a very significant impact on the composition and chemistry of the global atmosphere. Important atmospheric gases produced in the biosphere include oxygen (O_2), nitrous oxide (N_2O), nitric oxide (NO), methane (CH_4), and ammonia (NH_3). Photochemical calculations have been performed to assess the relationship between the magnitude of the biospheric source of these gases and their atmospheric abundance in the oxygen-free and later oxygen-evolving atmosphere. The evolution of oxygen in the atmosphere impacted the composition and chemistry of the atmosphere in several different ways: (1) Oxygen controlled the origin and evolution of atmospheric ozone (O_3), (2) Oxygen and ozone control the rates of molecular photolysis in the ultraviolet, and, hence, control many photochemical processes in the atmosphere, (3) Oxygen controls the oxidation state of the biosphere and, hence, controls the chemical nature of the production of gases, i. e., oxidizing vs. reducing gases, and (4) The origin of atmospheric oxygen led to the possibility of lightning-inducing fires, a significant source of many atmospheric gases, including carbon dioxide, carbon monoxide, methane, nonmethane hydrocarbons, and nitric oxide.

Theoretical calculations performed with a one-dimensional photochemical model have been performed to assess the biospheric-atmospheric transfer of gases. Ozone reached levels to shield the Earth from biologically lethal solar ultraviolet radiation (220-300 nm) when atmospheric oxygen reached about 1/10 of its present atmospheric level. In the present atmosphere, about 90 percent of atmospheric nitrous oxide is destroyed via solar photolysis in the stratosphere with about 10 percent destroyed via reaction with excited oxygen atoms. The reaction between nitrous oxide and excited oxygen atoms leads to the production of nitric oxide in the stratosphere, which is responsible for about 70 percent of the global destruction of oxygen in the stratosphere. In the oxygen-/ozone-deficient atmosphere, solar photolysis destroyed about 100 percent of atmospheric nitrous oxide, relegating the production of nitric oxide via reaction with excited oxygen to zero. Our laboratory and field measurements indicate that atmospheric oxygen promotes the biogenic production of N_2O and NO via denitrification and the biogenic production of methane by methanogenesis.

A WINDOW IN TIME FOR THE FIRST EVOLUTIONARY RADIATION

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The window in time between the last globally sterilizing event and the evidence for a complex procaryotic ecosystem is quite narrow, perhaps as small as 200 million years. We will present a heuristic model outlining the first evolutionary radiation that could have led from primordial vesicles to the universal ancestor. The concept of the universal ancestor will be developed in terms of contemporary molecular biology.

SESSION IV

EARLY EVOLUTION OF LIFE: THE BIOLOGICAL RECORD

Chairman - L. I. Hochstein

The evolutionary record occurs in two forms: as the familiar fossil record in rocks, in which phylogeny is deduced from morphology, and in the genome of extant organisms, where mutational events, which are the stuff of evolution, are expressed in sequences found in the organism's nucleic acids, or the gene products. The presentation in this Symposium which addressed the early evolution of life reflected studies at the level of the metabolic pathway; investigations of evoltuion at the structural and functional levels; and finally investigations at the molecular level with particular emphasis on sequence data obtained from proteins and nucleic acids.

L. Jahnke described studies on the evolution of oxygen-requiring metabolic systems. The transition between oxygen-independent and oxygen-dependent systems may correlate the evolution of these processes with the appearance of oxygen. Hopanoids (whose synthesis does not require oxygen and which are only found in prokaryotes) have been suggested to be evolutionary precursors of sterols (whose biosynthesis requires oxygen and are found in prokaryotic and eukaryotic cells). Methane oxidizing bacteria contain both of these cyclic triterpenes suggesting that these organisms may be useful for studying the evolution of the biosynthetic pathway for sterol synthesis. These studies characterized the relative distribution of the hopanoids and sterols within the complex membrane systems of the methane oxidizing bacterium, Methylococcus capsulatus, and the effect of temperature on the fatty acid and sterol composition of the cells. The sterol and fatty acid content decreased as the temperature was raised whereas the hopanoid content was unaffected suggesting that sterols and hopanoids affect membrane function by regulating membrane fluidity.

L.I. Hochstein reported on a continuation of his studies on the membrane-bound ATPase from the Archaebacterium Halobacterium saccharovorum. There are two major classes of proton-translocating ATPases: the so-called F-type (or ATP Synthases), which are associated with the cytoplasmic membranes of bacteria and the membranes from thylakoids and mitochondria; and the V-type (or vacuolar) which are found in the endomembranes systems which occur in Eukaryotic cells. These two classes of ATPases appear to have arisen from a common ancestral enzyme. It has been suggested that Archaebacterial ATPases are V-type ATPases, although this hypothesis is based on the data obtained from a single Archaebacterium, the sulfur-dependent acidophilic thermophile, Sulfolobus acidocaldarius. The studies from Hochstein's laboratory indicate that the ATPase from the extremely halophilic Archaebacterium, H. saccharovorum, possesses properties characteristic of F- and V-type ATPases and suggest that this enzyme may be an intermediate in the evolution of these two classes of proton-translocating ATPases.

J. Lanyi reported on a new research direction undertaken in his laboratory with respect to the retinal pigments found in the extremely halophilic bacteria. These pigments, which are exclusively found in the extreme halophiles, carry out a unique form of energy transduction in which light energy is converted into a chemical gradient of protons. This process represents a more primitive method of "photosynthesis" than the more commonly known chlorophyll-based system. J. Lanyi also reported on the successful cloning of the gene for halorhodopsin, a phototransducing pigment which is involved in chloride transport. Sequence comparison of the genes for bacteriorhodopsin and halorhodopsin from *H. halobium*, and halorhodopsin from *Natronobacterium pharaonis* indicate while there is considerable evolutionary distance between these genes, there is significant similarity. It was concluded that there has been strong selective pressure present during the evolution of these phototransducing pigments.

R. Buchanan described a phylogenetic scheme for the evolution of photosynthesis. The marker chosen, the thioredoxins, are small, photochemical reducible, proteins. There are 2 types, thioredoxin *f* and *m* which have different functional and structural properties. Amino acid sequence studies indicate significant homology between the *m*-type thioredoxins from plants and bacteria. Thioredoxin *f* appears distantly related to bacterial thioredoxin. A phylogenetic tree constructed for the thioredoxins indicated that those from bacteria and animals fall into discrete groups. The chloroplast thioredoxins show two patterns: one, the *m*-type, resembles thioredoxins from algae and bacteria. The *f*-type thioredoxin shows a close relationship to animal thioredoxins.

One issue to understanding how to use sequence data (either nucleic acid or protein) is related to the rate with which changes take place. George Fox described studies related to this issue with respect to the use of ribosomal RNA as molecular phylogenetic markers. The rationale considers that the nucleotide sequence of an RNA molecule reflects a particular function, and that such sequences represent one of many that may occupy a larger domain, or structure space. If RNA molecules within a structure space are homogeneous, the rate of evolution would predictably be uniform whereas if they are heterogeneously distributed, mutation rates would be dependent on sequence and mutations not be uniform. Preliminary experiments involved developing an artificial plasmid containing a 5s rRNA gene. A series of mutants were prepared for testing the relative homogeneity of a particular structure space.

R. Krestsinger described a comparison of a number of calcium-binding proteins. Analysis suggested that these calcium-binding proteins could be described by fourteen discrete groupings. The results of these studies indicate that the ability to bind calcium was lost and acquired a number of times. The rate of evolution of these proteins within the group appeared to be much slower than prior to the formation of the particular group.

J. Troust reported on studies whose goal is to characterize the early evolution of photosynthesis. The approach is to examine the photosynthetic reaction centers in an organism belonging to the genus *Heliobacterium* that contain the simplest known such centers. These reaction centers appear to have arisen from a progenitor that also gave rise to photosystem I which is found in oxygen-evolving photosynthetic organisms. The centers were isolated and were found to contain a peptide that bound photoreactive chlorophyll and bacteriochlorophyll g.

S. Fox summarized studies which implicate thermal proteins as possessing the ability to store and transfer biological information. The notion is that amino acids have an inherent self-sequencing capacity. Data was presented to account for the origin of the cells, including such essential characteristics as membranes and metabolic processes.

G. Hinkle presented information with respect to the hypothesis for the symbiotic origin of cilia, flagella, and the mitotic spindle from spirochetes.

The biological studies supported by the program in the early evolution of life are characterized by an increasing degree of sophistication. Although not at first obvious, a large number of the research projects are connected. The unifying theme is the evolution of energy-transducing systems as evidenced by the studies of chemical transducers (i.e. ATPases) and photochemical transducers (i.e. the retinal pigments of the extreme halophiles, the reaction centers of the heliobacter, and the diverse thioredoxins). Finally, G. Fox's studies are a novel approach directed toward a better understanding as to what determines the rate of mutation (i.e evolution).

THE EFFECTS OF OXYGEN ON THE EVOLUTION OF MICROBIAL MEMBRANES

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Extant microorganisms are an invaluable resource for furthering our understanding of Earth's evolution. Perhaps the greatest influence on this process has been the rise in levels of free oxygen. While the roots of biochemical pathways are anaerobic, oxygenase-type mechanisms did evolve once sufficient molecular oxygen was available. The products of these oxygen-requiring syntheses are more characteristic of eukaryotic organisms and must have been particularly important for the development of these more highly evolved cells. In a number of cases, examples of this evolutionary transition exist in extant prokaryotes and are of importance to furthering our understanding of cellular evolution. This is particularly true for the biosynthesis of sterols and hopanoids. With few exceptions. sterols are a ubiquitous constituent of eukaryotic membranes, however, only a few prokaryotes are known to synthesize them. Hopanoids, on the other hand, are present in many bacteria. Both compounds are cyclic triterpenes, products of the cyclization of squalene. While hopanoid synthesis is anaerobic, sterol synthesis involves several oxygen-requiring enzymes. Ourisson has suggested that hopane polyols are primitive analogues of the sterol molecule acting as membrane stabilizers, and, indeed, model membrane studies have suggested that hopanoids may perform a cholesterol-like function in bacterial membranes. One prokaryote, Methylococcus capsulatus, synthesizes both hopanoids and sterols and, thus, provides a unique opportunity to study the evolution of membrane function.

Methane-oxidizing bacteria, such as M. capsulatus, are characterized by the presence of three potentially distinct membrane systems: an outer, cell boundary layer; an inner or paricytoplasmic layer; and an extensive intracytoplasmic membrane system. When the outer and cytoplasmic membranes of this organism were separated by sucrose density centrifugation, lipid analysis showed that the sterol and hopane polyol (the principal hopanoid in this organism) were associated predominantly with the outer membrane. The molar ratio of phospholipid to hopane or sterol in the cytoplasmic membrane was approximately 30:1, similar to the ratio for whole cells. However, the ratios for outer membrane were 11:1 for hopane and 6:1 for sterol. When M. capsulatus was grown at different temperatures, lipid analysis of the whole cells showed that both sterol and unsaturated fatty acid levels decreased at higher growth temperatures; sterol concentrations were 0.116 μmole/μmole phospholipid at 30°C and 0.025 μmole/μmole phospholipid at 45°C, while the saturated to unsaturated fatty acid ratio increased from 0.397 to 1.475. Hopane polyol levels were constant over this temperature range, however, methylation of the A-ring (a characteristic modification of the hopane molecule in some methane-oxidizers) decreased markedly in cells grown at 30°C. These results imply that sterol and hopane molecules are required for enhancement of some specific membrane function, potentially by modulating membrane fluidity.

ON THE CHIMERICAL NATURE OF THE MEMBRANE-BOUND ATPASE FROM HALOBACTERIUM SACCHAROVORUM

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There is increasing evidence that proton translocating ATPases evolved from a progenitor that had the structural characteristics of vacuolar ATPases (V-ATPases) but, unlike this class of enzymes, was capable of synthesizing ATP. Interestingly, the Archaebacteria, a diverse collection of organisms that diverged from the Prokaryotes at an early stage in the evolution of life, possess ATPases more closely related to V-ATPases than to F_0F_1-ATPases(F-ATPases).

However, an antiserum against the "ß" subunit from S. acidocaldarius reacts with the ß subunit from an F-ATPase as well as subunit II from Halobacterium saccharovorum ATPase (subunit II is probably the functional equivalent to the ß subunit). This communication describes a series of experiments carried out with the goal of determining how the membrane-bound ATPase from H. saccharovorum is related to V- and F-type ATPases, and reflect three approaches: the use of inhibitors; structural studies; and immunological relatedness.

Nitrate is extremely useful for distinguishing between V- and F-ATPases since only the former are inhibited by this reagent. The enzyme from H. saccharovorum is also inhibited by nitrate and at concentrations that inhibit V-ATPases and ATPases from other Archaebacteria. N-ethylmaleimide, which inhibits V- and F-ATPases, also inhibits the ATPase from H. saccharovorum. However, whereas V-type enzymes are inhibited by µM concentrations of this reagent, F-type and the halobacterial enzyme are inhibited by mM concentrations of NEM. 4-chloro-7-nitrobenzofurazan, a nucleotide analog, inhibits V-, F-, and the halobacterial ATPases. In the case of the V-ATPases inhibition is accompanied by the binding of the inhibitor to the largest of the subunits, which is the catalytic subunit. 4-chloro-7-nitrobenzofurazan binds to the ß-subunit of F-ATPases, which is the catalytic subunit. 4-chloro-7-nitrobenzofurazan binds to subunit II of the halobacterial enzyme, which also contains the dicylcohexylcarbodiimide-binding site. In spite of this apparent similarity, the halobacterial enzyme is unrelated to F-type ATPases based on a comparison of the isoelectric points, the amino acid compositions, the molecular mass, and the proteolytic products of the two largest subunits from each enzyme. Furthermore, antisera prepared against the largest subunit from the V-ATPase from Neurospora crassa reacts with subunit I from the halobacterial enzyme. On the basis of these observations, the halobacterial enzyme may represent a chimera. Subunit II appears to be immunologically and functionally related to the ß subunit from F-ATPases. On the other hand, subunit I may be structurally related to the largest of the largest subunits from V-ATPases but possibly functionally related to the α-subunit from F-ATPases (which has a regulatory function). Whether this reflects the nature of the progenitor enzyme or mixture of structure and function which arose after the evolution of the proton ATPases into V- and F-type enzymes is not clear, but it is another example of the evolutionary richness of the extremely halophilic bacteria.

ARCHAEBACTERIAL RHODOPSIN SEQUENCES: IMPLICATIONS FOR EVOLUTION

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It has been proposed over 10 years ago that the archaebacteria represent a separate kingdom which diverged very early from the eubacteria and eukaryotes. It follows, therefore, that investigations of archaebacterial characteristics might reveal features of early evolution. Yet, the phylogeny of the archaebacteria and its constituent groups is still subject to controversy. Few archaebacterial genes which code for proteins, and could begin to help in deciding these important issues, have been sequenced so far. The bacterial rhodopsins are found in halophilic archaebacteria, and constitute a relatively well characterized group of membrane proteins. So far, two genes, one for bacteriorhodopsin and another for halorhodopsin, both from *Halobacterium halobium*, have been sequenced. We cloned and sequenced the gene coding for the polypeptide of another one of these rhodopsins, a halorhodopsin in *Natronobacterium pharaonis* (named here pharaonis halorhodopsin). Peptide sequencing of cyanogen bromide fragments, and immuno-reactions of the protein and synthetic peptides derived from the C-terminal gene sequence, confirmed that the open reading frame was the structural gene for the pharaonis halorhodopsin polypeptide. The flanking DNA sequences of this gene, as well as those of other bacterial rhodopsins, were compared to previously proposed archaebacterial consensus sequences. In pairwise comparisons of the open reading frame with DNA sequences for bacterio-opsin and halo-opsin from *Halobacterium halobium*, silent divergences (mutations/nucleotide at codon positions which do not result in amino acid changes) were calculated. These indicate very considerable evolutionary distance between each pair of genes, even in the dame organism. In spite of this, the three protein sequences show extensive similarities, indicating strong selective pressures.

THIOREDOXIN AND EVOLUTION

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Thioredoxins are a widely distributed group of small proteins with a conserved dithiol active site. Chloroplasts contain two types of thioredoxin (*f* and *m*) for which functional differences coincide with differences in structure. These thioredoxins, which are both reduced photochemically by way of ferredoxin and ferredoxin-thioredoxin reductase, regulate biochemical activity in chloroplasts in response to light by reducing specific target enzymes and changing their activities. Thioredoxin *f* preferentially activates enzymes of the photosynthetic carbon cycle (fructose bisphosphatase, sedohepulose bisphosphatase, phosphoribulokinase, NADP-glyceraldehyde 3-P dehydrogenase). Thioredoxin *m* preferentially activates an associated enzyme, NADP-malate dehydrogenase, and deactivates, also apparently by enzyme reduction, an enzyme of carbonate breakdown (glucose 6-P dehydrogenase). Both thioredoxins interact with CF1-ATPase, the enzyme forming ATP. Recently the regulatory thiol site has been identified for most of these enzymes. In each case, a specific disulfide (S-S) group is reduced to the sulfhydryl (SH) level, leading to the activation of the enzyme. This redox modulation enables chloroplasts to use light for the regulation of these enzymes, thereby achieving "biochemical order"--i.e., futile cycling is minimized so that starch can be built up in the light and broken down in the dark.

Comparisons of primary structure have revealed significant homology between the *m* type thioredoxins of chloroplasts and the thioredoxins from a variety of bacteria. Chloroplast thioredoxin *f*, by contrast, remains an enigma: certain residues are invariant with those of other thioredoxins, but a phylogenetic relationship to bacterial or *m* thioredoxins seems distant. Knowledge of the evolutionary history of thioredoxin *f* is, nevertheless, of interest because of its role in photosynthesis. We have, therefore, attempted to gain information on the evolutionary history of chloroplast thioredoxin *f*, as well as *m*. Our goal was first to establish the utility of thioredoxin as a phylogenetic marker, and, if found suitable, to deduce the evolutionary histories of the chloroplast thioredoxins. To this end, we have constructed phylogenetic (minimal replacement) trees using computer analysis. The results show that the thioredoxins of bacteria and animals fall into distinct phylogenetic groups--the bacterial group resembling that derived from earlier 16s RNA analyses and the animal group showing a cluster consistent with known relationships. The chloroplast thioredoxins show a novel type of phylogenetic arrangement: one (*m* type) aligns with its counterpart of eukaryotic algae, cyanobacteria and other bacteria, whereas the second (*f* type) tracks with animal thioredoxin. The results give new insight into the evolution of photosynthesis.

EXPLORATION OF RNA STRUCTURE SPACES

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Studies in molecular phylogeny have relied heavily on ribosomal RNAs to establish relationships between extant organisms and to identify the earliest branchings. These ribosomal RNAs are major components of the ribosomal machinery whose development was central in the early development of life. The role of RNA in early evolution may be even more general however, as even small RNAs have the potential to carry genetic information while exhibiting catalytic activity. At this stage it is essential to understand how an RNA molecule can respond to the evolutionary processes. This will provide insight to the reliability of early branching patterns detected in phylogeny studies and reveal how more complex structures can evolve from simpler ones.

RNA molecules of any particular function are perceived as a set of primary sequences that satisfy the biological conditions for that RNA. The set of such sequences for any particular RNA is a subset of sequence space that is referred to as structure space. Over evolutionary time, an RNA molecule explores its current structure space as long as it retains its biological function. Changes in function and/or increases in complexity require transition to a different structure space. In order to understand RNA evolution, it is essential to understand how the sequences comprising a typical structure space are related. If, for example, they are homogeneously distributed, then each has essentially the same number of equally accessible neighbors and the rate of the evolutionary process would be uniform. In contrast, in a heterogeneous structure space the probability of mutations being accepted is strongly dependent on current sequence and hence rates are not necessarily uniform.

In order to examine the structure of real structure spaces we are studying the 5S rRNA structure space experimentally. A plasmid containing a synthetic 5S rRNA gene, two rRNA promoters, and transcription terminators has been assembled. Assays are conducted to determine if the foreign 5S rRNA is expressed, and to see whether or not it is incorporated into ribosomes. Evolutionary competition is used to determine the relative fitness of strains containing the foreign 5S rRNA and a control 5S rRNA. By using site directed mutagenesis a number of mutants can be made in order to study the boundaries of the structure space and how sharply defined they are. By making similar studies in the vicinity of several points of structure space, it will be possible to determine how homogeneous the 5S rRNA structure space is. Useable experimental protocols have been developed, and a number of mutants have already been studied. Initial results suggest an explanation of why single stranded regions of the RNA are less subject to mutation than double stranded regions.

FUNCTIONAL CHARACTERISTICS OF THE CALCIUM MODULATED PROTEINS SEEN FROM AN EVOLUTIONARY PERSPECTIVE

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We have constructed dendrograms relating 173 EF-hand proteins of known amino acid sequence. The EF-hand, or calmodulin fold, consists of 29 amino acids -- 1-10 in helix E; calcium coordinating side chains 10 X, 12 Y, 14 Z, 18 -X, 21 -Z; and 21-29 in helix F. This homolog domain is present in from two to eight random repeats in (nearly) all calcium-modulated proteins in the cytosol. The intradomain regions are much more highly conserved than the interdomain regions. We aligned all of these proteins by their EF-hand domains, omitting interdomain regions. Initial dendrograms were computed by minimum mutation distance methods. Using these as starting points we determined the best dendrogram by the method of maximum parsimony, scored by minimum mutation distance.

We identified fourteen distinct subfamilies as well as six unique proteins (indented), perhaps the sole representatives of other subfamilies:

Name Ca-binding in Domains	1	2	3	4	5	6
Calmodulin	+	+	+/?	+/?		
Troponin C	+/-	+	+/-	+		
Troponin C (*Astacus*)	-	+	-	+		
Parvalbumin		-	+	+		
Calbindin	+	-	+	+	+	-
Calcineurin B	+	+	+	+		
S100	+/-	+/-				
Essential Light Chain of Myosin	+/-	-	+/-	+/-		
Calcium Vector Protein	-	-	+	+		
Regulatory Light Chain of Myosin	+	-	-	-		
Caltractin & CDC31	+	+/-	+/-	+		
Stronglyocentrotus ectodermal prot.	+	+/?	+/?	+		
α- Actinin	+/-	+/-				
25 kDa Protein (*Tetrahymena*)	+	+	?	+		
Ca-binding protein (*Lytechinus*)	+	+	+	+		
Sarcoplasm Ca-binding Protein	+	+/-	+/-	+/-		
Ca-binding Protein (*Streptomyces*)	+	?	+	+		
Aequorin	+	-	+	+		
Calpain	+	+	-	-		
Ca-binding Protein (*Canis* thyroid)	+	+	+	?		

Within subfamilies, one can easily align interdomain regions. The resulting dendrograms are very similar to those computed using domains only. Dendrograms constructed using pairs of domains show general congruence. However, there are enough exceptions to caution against an overly simple scheme in which a pair of gene duplications leads from a one domain precursor to a four domain prototype from which all other forms evolved. The ability to bind calcium was lost and acquired multiple times during evolution.

The distribution of introns does not conform to the dendrogram based on amino acid sequences.

The rates of evolution appear to be much slower within subfamilies, especially within calmodulin, than those prior to the definition of subfamily.

PHOTOSYNTHETIC REACTION CENTER COMPLEXES FROM HELIOBACTERIA

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Photosynthetic reaction centers are pigment-protein complexes that are responsible for the transduction of light energy into chemical energy. Considerable evidence indicates that photosynthetic organisms were present very early in the evolution of life on Earth. The goal of this project is to understand the early evolutionary development of photosynthesis by examining the properties of reaction centers isolated from certain contemporary organisms that appear to contain the simplest photosynthetic reaction centers. The major focus of this project is the family of newly discovered strictly anaerobic photosynthetic organisms known as Heliobacteria. These organisms are the only known photosynthetic organisms that are grouped with the gram-positive phylum of bacteria. The properties of these reaction centers suggest that they may be the descendants of an ancestor that also gave rise to Photosystem I found in oxygen-evolving photosynthetic organisms.

Photoactive reaction center-core antenna complexes have been isolated from the photosynthetic bacteria *Heliobacillus mobilis* and *Heliobacterium gestii* by extraction of membranes with Deriphat 160C followed by differential centrifugation and sucrose density gradient centrifugation (Trost and Blankenship, Biochemistry 28, 9898-9904, 1989). The purified complexes contain one or more 48,000 Mr peptides that bind both the photoactive chlorophyll P800 and approximately 25 molecules of antenna bacteriochlorophyll *g*. Time-resolved fluorescence spectroscopy indicates that the antenna pigment are active in energy transfer to P800, exhibiting a major decay time of 25 ps in both membranes and reaction centers. The absorption and fluorescence properties of membranes and reaction centers are almost identical, suggesting that a single pigment-protein complex serves as both antenna and reaction center. Experiments in progress include sequence determination of the 48,000 Mr reaction center protein, and evolutionary comparisons with other reaction center proteins. These experiments are being done using chemical sequencing methods to obtain a partial sequence, followed by oligonucleotide synthesis and DNA hybridization to obtain the gene(s) for the protein(s).

MOLECULAR BASES FOR UNITY AND DIVERSITY IN ORGANIC EVOLUTION

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The origin of biological information on the Earth has been ascribed at various times to DNA, RNA, or protein. The origin of nucleic acids without the action of prior informed protein has not been supported by plausible experiments, although such possibilities have been examined (e. g. Schwartz and Fox, 1964). DNA synthesis has been assigned to a distant unnamed planet (Crick, 1981). The fallacies of concepts involving RNA in this context, despite demonstrated catalytic activity (Cech, 1983), have been reviewed by Waldrop (1989) and Fox (1984).

The one experimentally based explanation for the origin of biological information is the endogenously ordered synthesis of thermal proteins due to the stereoelectronic specificities of the types of precursor amino acid (Fox and Dose, 1972). This method of selfsequencing of amino acids and its results have been described in numerous reports (summaries in Fox, 1981; Dose, 1984; Melius, 1982). Moreover, Ivanov and Foertsch (1986) have accumulated data from the Martinsried protein primary sequence data bank that indicate the selfsequencing of amino acids is part of the ordering mechanism in modern protein synthesis.

The behavior of the thermal proteins and of the microspheres selfassembled therefrom explain the origin of the first cells, the first membrane, the first reproduction cycle, ancient metabolism including ATP-aided syntheses of peptides and polynucleotides, growth, bioelectricity, and of polybiofunctionality in general (Fox, 1980, 1989). Closer study of the products of heating mixtures of amino acids may explain evolutionary origins of unity and diversity in thermal proteins and in organisms.

+ Deceased, 1989

SEDIMENTARY ORGANIC MOLECULES: ORIGINS AND INFORMATION CONTENT

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Improved knowledge of ancient redox levels and of CO_2 abundances is crucial to correct reconstruction of earth's environmental history. Much relevant information must be encoded in the sedimentary record of organic carbon. The presence of organic material in sediments is commonly considered in terms of "preservation," in the sense that some organic debris has escaped recycling. That ultimately immobilized in sedimentary rocks, however, is the product of an ecosystem devoted to utilization - *not* preservation - of organic material. Although it is interesting to think in terms of the fraction of primary organic carbon that winds up in sedimentary rocks, use of the primary production as the reference point directs attention away from most of the action. Nearly all carbon-carbon bonds established in primary production are broken as plant products and utilized within the food chain. Organic geochemistry, sometimes described as "molecular paleontology," deals with the complex mixture of products deriving from these processes. Each organic compound represents only a tiny part of the parent organism. Extending the analogy, we must acknowledge that the fossils have been disarticulated and scrambled.

To progress, we must dissect the processes controlling the composition of sedimentary organic matter. Structurally, this has proven difficult. Individual "biomarkers" can often be recognized, but their contribution to total organic matter is small, and their presence does not imply that their biochemical cell mates have survived. We are finding, however, that a combination of structural *and* isotopic lines of evidence provides new information. A starting point is provided by the isotopic compositions of primary products (degradation products of chlorophylls, alkenones derived from coccoliths). We find strong evidence that the isotopic difference between primary carbonate and algal organic material can be interpreted in terms of the concentration of dissolved CO_2. Moreover, the isotopic difference between primary and total organic carbon can be interpreted in terms of characteristic isotopic shifts imposed by secondary processes (responsive, for example, to O_2 levels in the depositional environment). In favorable cases, isotopic compositions of a variety of secondary products can be interpreted in terms of flows of carbon, and, therefore, in terms of specific processes and environmental conditions within the depositional environment.

EARLY ARCHEAN STROMATOLITES: PALEOENVIRONMENTAL SETTING AND CONTROLS ON FORMATION

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The earliest record of terrestrial life is contained in thin, silicified sedimentary layers within enormously thick, predominantly volcanic sequences in South Africa and Western Australia. This record includes bacteria-like microfossils, laminated carbonaceous structures resembling flat bacterial mats and stromatolites, and a morphologically diverse assemblage of carbonaceous particles. These structures and particles and their host sediments provide the only direct source of information on the morphology, paleoecology and biogeochemistry of early life; the nature of interactions between organisms and surface systems on the early earth; and possible settings within which life might have evolved.

The three known occurrences of 3.5 to 3.2 billion-year-old stromatolites have been evaluated in terms of depositional setting and biogenicity. All occur within sedimentary units deposited in shallow, probably marine waters on large, low-relief, oceanic volcanic platforms. Hawaii provides perhaps the best modern analog. Evaporitic sediments are common components of these sequences. Associated, off-platform, deep-water deposits commonly contain abundant detrital carbonaceous matter but appear to lack in situ bacterial mats or stromatolites. This environmental specificity of early bacterial communities represents perhaps the most convincing evidence yet reported that they included photosynthetic organisms. The morphology of small conical stromatolites in the Strelley Pool Chert, Western Australia, appears to have been controlled mainly by precipitative processes in hypersaline waters. The well-known stromatolite from the North Pole, Western Australia, consisting of a single specimen that includes one partial stromatolite, probably represents a chunk of flat bacterial mat deformed by soft-sediment movement and the post-depositional growth of evaporitic carbonate or gypsum nodules. Stromatolites in the Barberton Greenstone Belt, South Africa, formed at least in part by inorganic precipitation and resemble siliceous sinter. They apparently developed by silica precipitation in wave- and current-active shallow-water areas fringing the volcanic platforms. Although all of these early Archean stromatolites appear to have been formed at least in part by inorganic, commonly precipitative processes, there is also some evidence that they were covered by active bacterial mats during growth. This may simply reflect passive biological opportunism. It seems plausible, however, that the surficial mats played an important role in controlling local microenvironments and influencing if not mediating precipitation. This could reflect a more active strategy involving the coupling of biological and inorganic processes to produce structures on the shallow sea floor that enhanced community survival.

EARLY ARCHEAN (~3.4 Ga) PROKARYOTIC FILAMENTS FROM CHERTS OF THE APEX BASALT, WESTERN AUSTRALIA: THE OLDEST CELLULARLY PRESERVED MICROFOSSILS NOW KNOWN

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In comparison with that known from later geologic time, the Archean fossil record is miniscule: although literally hundreds of Proterozoic formations, containing more than 2800 occurrences of bona fide microfossils, are now known, fewer than 30 units, containing some 43 categories of putative microfossils (the vast majority of which are of questionable authenticity), have been reported from the Archean. Among the oldest fossils now known are Early Archean filaments reported from cherts of the Towers Formation (Awramik et al., 1983) and the Apex Basalt (Schopf and Packer, 1987) of the 3.3-3.6 Ga-old Warrawoona Group of Western Australia. The paleobiologic significance of the Towers Formation microstructures is open to question: thin aggregated filaments described by Awramik et al. are properly regarded as "dubiomicrofossils" -- perhaps biogenic, but perhaps not -- and they therefore cannot be regarded as firm evidence of Archean life. And although authentic, filamentous microfossils were reported by Awramik et al. from a second Towers Formation locality, because the "precise layer" containing the fossiliferous cherts "has not been relocated" (Awramik et al., 1983, 1988), this discovery can neither be reconfirmed by the original collector nor confirmed independently by other investigators.

Discovery of microfossils in bedded cherts of the Apex Basalt (Schopf and Packer, 1987), the stratigraphic unit immediately overlying the Towers Formation, obviates the difficulties noted above. The cellularly preserved filaments of the Apex Basalt meet all of the criteria required of bona fide Archean microfossils: (i) they occur in rocks of unquestionably Archean age; (ii) they are demonstrably indigenous to these Archean sediments; (iii) they occur in lithic clasts that are assuredly syngenetic with deposition of this sedimentary unit (with the fossils themselves pre-dating deposition of the bedded cherts in which the clasts occur); (iv) they are certainly biogenic; and (v) as demonstrated by replicate sampling of the fossiliferous outcrop, the provenance of these microfossils is known with certainty. Recent studies indicate that the Apex assemblage includes at least six morphotypes of uniseriate filaments, composed of barrel-shaped, discoidal, or quadrate cells and exhibiting rounded or conical terminal cells and medial bifurcated and paired half-cells that reflect the occurrence of prokaryotic binary cell division. Interestingly, the majority of these morphotypes are morphologically more similar to extant cyanobacteria than to modern filamentous bacteria. Prokaryotes seem clearly to have been "hypobradytelic," exhibiting exceptionally slow rates of morphological evolutionary change, and the evidence suggests (but does not prove) that physiologically advanced oxygen-producing photosynthesizers may have been represented in the Early Archean biota.

THE ENVIRONMENTAL DISTRIBUTION OF LATE PROTEROZOIC ORGANISMS

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Along present day coast lines, the environmental distributions of prokaryotic and protistan populations are often sharply delimited. Realized habitat ranges are generally narrower than those circumscribed by physiological tolerances, suggesting the importance of organism-organism interactions in the determination of population distributions. Microfossil populations preserved in silicified carbonates, dolomites, and shales of the 700-800 Ma old Akademikerbreen Group, Svalbard, and elsewhere indicate that the environmental distributions were defined equally clearly during the Proterozoic Eon. The Draken Conglomerate Formation is a tidal flat/lagoonal complex in which we have distinguished five principle biofacies containing a total of 42 taxa. Supratidal to subtidal gradients include the increasing abundance and diversity of both mat dweller microbenthos and allochthonous (principally planktonic) organisms, as well as a taphonomically important pattern of decreasing sheath thickness among mat builder microorganisms. The seaward barriers of Akademikerbreen lagoons were oolitic shoals, and these contain about a dozen endolithic and epilthic species not observed elsewhere in the group. Subtidal environments below fair weather wave base are represented by mudstones of the Svanbergfjellet Formation. These contain abundant and diverse cyanobacteria-like fossils generally similar to but specifically different from those found in tidal flat sediments, as well as diverse unicellular protists -- some of impressive morphological complexity -- and at least half a dozen cellularly preserved metaphyte populations. In all, more than 80 species are distributed among Akademikerbreen lithologies. Fossil assemblages from Svalbard and elsewhere illustrate the potential for a much finer paleoecological, biostratigraphic, and, hence, evolutionary resolution of the early fossil record.

THE BIOGEOCHEMISTRY OF MICROBIAL MATS, STROMATOLITES AND THE ANCIENT BIOSPHERE

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Stromatolites offer an unparalleled geologic record of early life, because they constitute the oldest (3.5 Ga) and most abundant recognizable remains of microbial ecosystems. Microbial mats are living homologs of stromatolites, thus we can study the physiology of the microbiota as well as the processes which create those features of mats (e.g., "biomarker" organic compounds, elemental and stable isotopic compositions) which are preserved in the ancient record.

Our observations of the carbon isotopic composition ($\partial^{13}C$) of stromatolites and microbial mats are consistent with the hypothesis that atmospheric CO_2 concentrations have declined by at least one to two orders of magnitude during the past 2.5 Ga. Whereas $\partial^{13}C$ values of carbonate carbon average about 0 permil during both the early and mid-Proterozoic, the $\partial^{13}C$ values of stromatolitic organic matter increase from an average of -35 between 2.0 and 2.6 Ga ago to an average of about -28 about 1.0 Ga ago. Modern microbial mats in hypersaline environments have $\partial^{13}C$ values typically in the range of -5 to -9, relative to an inorganic bicarbonate source at 0 permil. Both microbial mats and pure cultures of cyanobacteria grown in waters in near-equilibrium with current atmospheric CO_2 levels exhibit minimal discrimination against ^{13}C. In contrast, hot spring cyanobacterial mats or cyanobacterial cultures grown under higher CO_2 levels exhibit substantially greater discrimination. If care is taken to compare modern mats with stromatolites from comparable environments, it might be possible to estimate ancient levels of atmospheric CO_2.

In modern microbial mats a tight coupling exists between photosynthetic organic carbon production and subsequent carbon oxidation, mostly by sulfate reduction. The rate of one process fuels a high rate of the other, with much of the sulfate reduction occurring within the same depth interval as oxygenic photosynthesis. That sulfate reduction activity occurs within a well-oxygenated environment questions the conventional view that this is an obligately anaerobic process. Also contrary to conventional thought, appreciable isotopic discrimination is observed even at the highest rates of sulfate reduction (>12 millimolar per day). The sulfide has an isotopic composition ($\partial^{34}S$) about 45% lighter than that of the sulfate from which it is produced. This large isotopic discrimination might allow us to search for the evolution of sulfate reduction as a carbon mineralization process in stromatolites. This process was indeed an important addition to the cycling of carbon on the early earth.

SYMBIOSIS AND THE ORIGIN OF EUKARYOTIC MOTILITY

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Our work continues to test the hypothesis of the origin of eukaryotic cell organelles by microbial symbioses. With the widespread acceptance of the serial endosymbiotic theory (SET) of the origin of plastids and mitochondria, we are testing the novel idea of the symbiotic origin of the centrioles and axonemes (i. e., kinetosomes [9(3) + 0]*; undulipodia including cilia, eukaryotic 'flagella' and all [9(2) + 2] organelles; the mitotic spindle, and other eukaryotic microtubular systems) from spirochete bacteria motility symbioses. Intracellular microtubular systems are purported to derive from symbiotic associations between ancestral eukaryotic cells and motile bacteria. We are pursuing four lines of approach to this problem: cloning the gene of a tubulin-like protein we discovered in *Spirocheata bajacaliforniensis*, seeking axoneme proteins in spirochetes by antibody cross-reaction, attempting to cultivate larger, free-living spirochetes and studying in detail spirochetes (e. g., *Cristispira*) symbiotic with marine animals.

The recent discovery of megabase quantities of DNA in the kinetosomes (the structures underlying all undulipodia) of the green alga *Chylamydomonas reinhardtii* by Hall, Ramanis and Luck [Cell (1989) 59:121-132] has brought our still-controversial hypothesis to the fore of a long-standing, newly intensified debate within the cell biology community on the origin of microtubules in eukaryotic cells. While we await confirmation of Hall's *et al.* report on the presence of a third extranuclear genome (complementary to the genomes of plastids and mitochondria), we plan to probe the spirochete genomic DNA with kinetosome-specific DNA probes in hopes of finding homologous sequences. Regardless of the presence or absence of spirochete-kinetosome DNA homologies, the existence of an extranuclear genome within the elemental structure of eukaryotes, i. e., the kinetosome, is strong circumstantial evidence for an autonomous, symbiotic origin for eukaryotic microtubule-based motility systems.

*-The numbers between brackets refer to the arrangement of 24nm microtubules as seen in transverse electron-microscopic section of these structures.

IS CO_2 CAPABLE OF KEEPING EARLY MARS WARM?

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One of the goals of NASA's Exobiology Research Program is to determine whether life exists today on Mars (unlikely) or whether it might have existed there at some time in the past (more likely). Speculation about extinct life is driven by the observation of channels on the Martian surface, thought to indicate the past presence of liquid water and, hence, the existence of a warmer climate. Current thinking suggests that such a climate could have been maintained if early Mars had a dense CO_2 atmosphere with a surface pressure of 1 to 5 bars.

One of the phenomena that Martian climate modelers (including myself) have not looked at very carefully is the process of CO_2 condensation. Reexamination of some of my own calculations indicates that condensation should occur at high altitudes in some high-CO_2, Martian atmospheres, particularly those in which the solar constant is set to its initial main sequence value, about 70% of present. CO_2 condensation should affect the surface temperature in at least two ways: 1) If it occurs in the convective lower atmosphere, condensation will reduce the magnitude of the greenhouse effect by decreasing the lapse rate. 2) Condensation at any altitude will produce clouds, which can either warm or cool the climate depending on their altitude and optical depth. (The dominant effect, however, is likely to be cooling.) Preliminary calculations with a one-dimensional, radiative-convective climate model indicate that the lapse rate change is substantial for low solar luminosity models. Indeed, the calculations imply that no amount of CO_2 is capable of raising the mean surface temperature of early Mars above the freezing point of water, because the increase in planetary albedo due to Rayleigh scattering outstrips the greenhouse effect at high CO_2 partial pressures! These calculations are preliminary and do not take into account changes in cloudiness (which may worsen matters) or the nonideal behavior of CO_2 along its saturation vapor pressure curve (effect not yet determined). More detailed calculations are presently being performed. If this climate problem persists, then the question of what kept early Mars warm may need to be reexamined.

NONMARINE STROMATOLITES AND THE SEARCH FOR EARLY LIFE ON MARS

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The available evidence permits one to conclude that streams flowed and lakes developed on Mars sometime in the remote past. Speculating that (1) biopoesis occurred on Mars during its earliest history, (2) life evolved and diversified, (3) life inhabited aqueous environments, and (4) sunlight was an important environmental resource, then the lessons learned from the Earth's earliest fossil record suggest that stromatolites might have formed on Mars. The most likely place to find stromatolites and possibly microbial fossils on Mars would be in ancient lake and stream deposits. If thermal spring deposits can be identified, then they too are sites for biogeological investigations.

Today, lakes and thermal springs are not uncommon sites for stromatolites. This appears to be true for the Phanerozoic. However, for the pre-Phanerozoic, little is known about the record of life in nonmarine settings. Understanding the Archean and Proterozoic record of nonmarine stromatolites is important for the general understanding of the diversity of habitats for early life on Earth, sites of prokaryote evolution and diversification, and biogeological interactions through time. The possibility that a number of Archean and Proterozoic stromatolites might be nonmarine rather than marine has commonly been overlooked. Unfortunately, recognition of pre-Phanerozoic nonmarine deposits is difficult and ambiguous. Unlike pre-Phanerozoic marine stromatolites which formed in peritidal to slope environments with submerged carbonate platform settings apparently favoring luxuriant stromatolite development, lacustrine stromatolites may have developed best in near-shore settings. Morphological variability may be greater in nonmarine stromatolites. Thus, environmentally and morphologically, some nonmarine stromatolites may be distinctive. Favored environments for formation of Archean and Proterozoic lacustrine stromatolites and knowledge of their size, shape, and other morphological attributes are important for the search for evidence of ancient Martian life.

ENDOLITHIC MICROBIAL MODEL FOR MARTIAN EXOBIOLOGY: THE ROAD TO EXTINCTION

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Florida A&M University
and
E. I. Friedmann
Florida State University

Martian exobiology is based on the assumption that on early Mars, liquid water was present and that conditions were suitable for the evolution of life. Assuming that this was the case, two questions arise:

(1) How did life disappear from the surface?
(2) What recognizable fingerprints of past microbial activity could have been preserved on Mars?

(1) The Antarctic cryptoendolithic microbial ecosystem is a model for extinction in the deteriorating Martian environment. Laboratory measurements and computer analysis of long-term satellite-mediated nanoclimate records indicate that individual organisms live permanently near the lower limits of their temperature range (between -10°C and +2°C) while their optima are between 15°C and 25°C. In contrast, the net photosynthetic activity of the community shows a maximum around 0°C, reflecting the ambient temperature range. This apparently paradoxical situation is a result of a shift in the primary producer/consumer ratio, an adaptive response of the community. As the organisms are pushed to the limit of their physiological adaptability, even slight further deterioration in the environment (cooling) results in cell death. Such cases have been observed in nature. Thus, the response of organisms to extreme environmental pressures which result in extinction can be studied on this model at the cellular, organismal and community levels.

(2) Extreme dry environments are not conducive for fossilization. Yet, both Antarctic and hot desert endolithic microorganisms leave behind recognizable trace fossils in rocks. These trace fossils are the result of microbial leaching and of characteristic biogenous weathering patterns. Similar fingerprints of past microbial activity may also have been preserved on the surface of Mars.

THE NASA PLANETARY BIOLOGY INTERNSHIP EXPERIENCE

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By providing students from around the world with the opportunity to work with established scientists in the fields of biogeochemistry, remote sensing and origins of life, among others, the NASA Planetary Biology Internship (PBI) program has successfully launched many scientific careers. Begun in 1980, the PBI program has sponsored 100 interns in the past decade in over 50 different laboratories studying the effects of life on Earth at a planetary scale. The PBI program (from 1980-1986) has been described in the NASA document "The Internship Experience."

Each year approximately ten interns participate in research related to planetary biology at NASA centers, NASA-sponsored research in university laboratories, and private institutions. The PBI program also sponsors three students every year in both the Microbiology and Marine Ecology Summer courses at the Marine Biological Laboratory in Woods Hole, Massachusetts. The internships are open to all graduate students and senior undergraduates accepted in graduate programs regardless of nationality and generally last 6-8 weeks. In stressing the truly global nature of PBI, we have awarded approximately one-fifth of the internships in recent years to students from outside the United States. The internship consists of an award of $2000 in addition to a $1200 travel stipend (for 1990). In an area of fiscal constraints, the PBI program is rare in awarding young scientists travel funds and access to NASA supported research. These unparalleled opportunities have led to an increase in both the quality and number of the applicants every year.

The PBI program is supported by the Life Sciences Division of NASA and is administered by the Marine Biological Laboratory at Woods Hole, Massachusetts through the MBL Education Committee. Applications are due the 1st of March, 1991, and can be obtained from Gregory Hinkle, Department of Botany, University of Massachusetts, Amherst, MA 01003.

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SESSION V

EVOLUTION OF ADVANCED LIFE

Chairman - J. Billingham

This session covered research being carried out on asteroid impacts and their role in the great extinctions of the Phanerozoic Eon. F. Asaro, of the Lawrence Berkeley Laboratory reported on the "Fine Structure of the Late Eocene Iridium Anomaly in Marine Sediments". Iridium (Ir) anomalies due to the impact of asteroids or comets on the Earth had previously been identified in sediments from nine Late Eocene (approx. 35 million year old) sites, all at low latitudes. If the explosion from the impacting bodies were large enough to spread IR and other impact debris world-wide, then the impact debris could have obscured the sunlight and resulted in major extinctions of species. In this context it was important to know whether the late Eocene Ir anomalies also existed at high latitudes. If, in addition, there were clusters of impacts, then the Ir abundance profiles in the sediments might exhibit secondary peaks (fine structure) which would be separated by the same number of years from the main peak in each section (if the sedimentation rates were very well behaved). Such consistent fine structure would be supportive of the comet cluster hypotheses for impact on the Earth and also provide very accurate relative dating between sections.

The Iridium Coincidence Spectrometer was used to make detailed Ir profile measurements of three high-latitude Late Eocene marine sections from the Tasman Sea (36°S), the Weddell Sea (64°S) and the Massignano section in Italy (43°N). The most extensive measurements (over 400) were made in the Weddell Sea section, and only one Ir anomaly above 50 parts-per-trillion (ppt) was found in a continuous sampling of 5 million years of deposition. In each section there was a main Ir anomoly of 150 to 200 ppt which was not related to clay or other terrestrial abundances and hence could have been caused by the impact of an asteroid or comet on the Earth. Two and possibly all three sites exhibited shoulders below the main Ir peak of 13 to 27 ppt and another Ir peak of 17 to 27 ppt about 1 to 3 meters above the main peak.

Further work is planned to examine whether the main Ir peak in all three sections represents the same impact and, if so whether the secondary Ir peaks are due to separate impacts.

D. Rays, from the University of Chicago examined the critical role played by species extinction in the evolution of advance life on Earth. Without extinction, complex (and intelligent) organisms would probably not have developed. If we are to be successful in the search for extraterrestrial life, it is important to understand the role of extinction and to be able to recognize the physical conditions that cause extinction of species.

An analysis of Sepkoski's compendium of the geologic time ranges of 30,000+ genera of fossil animals has yielded a cumulative frequency distribution of species extinctions for the past 600 million years. This distribution, in the form of a "Kill Curve", gives the mean waiting-time between extinction events of a given magnitude. Thus, for example, events causing the extinction of 5% of existing species occur, on average, every one million years, while events causing 65% extiction occur about every 100 million years.

The equation for the Kill Curve has been combined with the most recent estimates of comet and asteroid impact rates to produce a curve that predicts the species kill that would result from a large-body impact if impact has been the primary cause of extiction of species in the past. The resulting curve is plausible and conforms to available information on the killing effects of impact. This leads, therefore, to the working hypothesis that impact is responsible for most species extinctions.

A new database on the geographic distribution of extinctions in the Cretaceous period has been constructied and analysed to search for geographic patterns in the mass extinction that ended the Cretaceous period. This is part of a larger project in database development to evaluate various strategies of building databases from the scientific literature.

One hundred eighty six previously published lists of fossil species and genera were analysed. Each list represents the fossils found at a geologic locality of latest Cretaceous age. The locations were converted electronically to their Cretaceous positions (to correct for continental drift). Multivariated analysis of the converted data shows clearly mappable biogeographic provinces, thus confirming the quality of the database.

For each fossil fauna, an extinction rate for genera was computed by comparison with Sepkoski's range data for the same fossil groups. The resulting map of extinction rates indicates that organisms in northern, mid-latitudes suffered substantially greater extinction than elsewhere. Any causal mechanisms proposed for the mass extinction must be consistent with this geographic pattern.

The fossil record on evolution was discussed by J. Sepkoski, also from the University of Chicago. He described the data he has assembled on diversification and extinction. Understanding the evolution of complex life is dependent upon knowledge of the fossil record. Sepkoski has been compiling a synoptic database on some 32,000 fossil genera from the international paleontologic literature. These data are being used to investigate the history of global biodiversity, to measure rates of evolution, and to test the 26 million year periodicity of mass extinction, a pattern that has become more pronounced as better data have been accumulated. Measured rates of extinction are also being used to parameterize models of evolutionary radiations and faunal change. It has been observed that new animal groups tend to expand first in stressed environments and then to radiate into more stable environments. The model suggests this will happen only if the new groups are characterized by species that are more successful in weathering normal environmental perturbations than the older groups being replaced. This same pattern is observed at periodic mass extinctions: groups that are normally characterized by low rates of extinction preferentially survive the abnormal times of mass extinction. Thus, the evolution of extinction resistance has been a key factor in the history of complex life.

The last paper entitled "Biogeochemical Modeling at Mass Extinction Boundaries: Atmospheric Carbon Dioxide and Ocean Alkalinity at the K/T Boundary".was given by

M. Rampino of the Goddard Institute for Space Studies. His co-author was K. Calderia of New York University.

The causes of mass extinctions and the importance of major bio-events in the history of life are subjects of scientific interest. A large amount of geological, geochemical, and paleontological information now exists for the Cretaceous/Tertiary (K/T) boundary (66 Myr BP). These data are used here to constrain a newly developed time-dependent biogeochemical cycle that is designed to study transient behavior of the Earth system.

Model results suggest that the rate of pelagic production of $CaCO_3$ shells during the low productivity Strangelove ocean period (66.5-66 Myr BP) should have fallen below the rate of riverine supply of Ca^{++} and Mg^{++} ions to the world ocean by about a factor of two. These results are supported by the observed low accumulation rates of $CaCO_3$ at a number of DSDP and ODP drill sites. Without the flux of $CaCO_3$ to the sediments, ocean alkalinity should have increased, resulting in a decrease of atmospheric CO_2, lowering of the $CaCO_3$ lysocline, and leading to a calculated global cooling of about 4.5°C for several hundred thousand years. Eventual return of ocean productivity and increased rock weathering would have decreased ocean alkalinity, and released CO_2 to the atmosphere causing a calculated warming of about 2°C over latest Cretaceous values. Strontium (Sr) isotope data suggest an increasing weathering flux to the oceans at the K/T boundary (possible warming and cooling), but the interpretation of these data is complicated by diagenesis and other effects. It is also possible that some stabilizing feedback may have acted to reduce the variability in ocean alkalinity, and hence atmospheric CO_2 during the Strangelove period. One possibility is that nutrient-rich waters may have led to increased rates of carbonate and organic precipitation in shallow waters, decreasing ocean alkalinity.

It was clear from the reports of all the authors that evidence for major body impact events is now becoming strong, and that their proposed role in the great extinction of evolutionary biology is gaining ground.

FINE STRUCTURE OF THE LATE EOCENE IR ANOMALY IN MARINE SEDIMENTS

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Lawrence Berkeley Laboratory, University of California, Berkeley

The following studies are part of a collaboration with several other scientists. The Late Eocene Ir abundance profile in deep sea cores from Ocean Drilling Program Leg 113 Hole 689B on the Maude Rise off of Antarctica was studied with 410 samples (encompassing about 5 million years of accumulation) which were collected continuously in 10 cm increments and measured with the Iridium Coincidence Spectrometer (ICS). The ICS was subsequently modified to measure 13 other elements simultaneously with the Ir. The abundance profiles of these elements were then determined in the Late Eocene Massignano section in central Italy with 250 samples (encompassing roughly 2 million years of accumulation) which were collected about every 5 cm in about 2 cm increments. These studies augmented a previous one (which included many elements) of deep sea cores from Deep Sea Drilling Project Site 592 on the Lord Howe Rise in the Tasman Sea between Australia and New Zealand. In the latter study 50 samples (encompassing roughly 0.7 million years of accumulation) were collected continuously in 10 cm increments.

In all three studies one major Ir anomaly, spread over 25 or more cm, was found with respective net abundances in parts-per-trillion (ppt) of 156±10 over an average background of 5.9±1.8, 156±19 over an estimated average background of 42.5±1.2 and 191±6 over an average background of 8.5±0.3. The respective positions of the main peaks were ODP 113-689B 14H-6, 100-110 cm; 5.61 meters (about 7.9 meters below the top of combined nannoplankton zone 19/20) based on the field meter markers in the Massignano section; and DSDP 90-592 38-5 50-60 cm (about 14.4 meters below the top of combined nannoplankton zone 19/20). The main Ir peak had a shoulder on the lower side which had net abundances of 13±5, 27±6 and 27±2 ppt, respectively, and was separated from the main peak by about 30, 17 and 30 cm, respectively. The precision of the first measurement was not good enough to be sure the peak was real. In two of the sections, Massignano and Site 592, another Ir peak was observed 131 and 220 cm respectively, above the main peak with respective net abundances of 27±5 and 19.2±1.5 ppt. A possible similar peak with a net Ir abundance of 17±7 ppt over a background of 6 ppt was observed in Hole 689B samples 330 cm above the main peak. The ICS was operating in a scanning mode in that region, however, and the precision of the measurement was not good enough to be certain the peak was real. The main Ir peaks tail upward in the three sections, and the tails may contain additional structure. An isolated sample at 10.24 meters in the Massignano section had an unusually high Ir abundance (313 ppt) and a Se abundance 200 times higher than the samples above and below.

The ramifications of the data with respect to relative chronology and relative sedimentation rates at the different sites and implications with respect to the comet cluster hypotheses of periodic impacts on the Earth will be discussed.

CUMULATIVE FREQUENCY DISTRIBUTION OF PAST SPECIES EXTINCTIONS

D. M. Raup*
University of Chicago

Analysis of Sepkoski's compendium of the time ranges of 30,000+ taxa yields a mean duration of 28.4 ma for genera of fossil invertebrates. This converts to an average extinction rate of 3.5 percent per million years or about one percent every 286, 000 years. Using survivorship techniques, these estimates can be converted to the species level, yielding a Phanerozoic average of one percent species extinction every 40,000 years.

Variation in extinction rates through time is far greater than the null expectation of a homogeneous birth-death model and this reflects the well-known episodicity of extinction -- ranging from a few large mass extinctions to so-called background extinction. The observed variation in rates can be used to construct a cumulative frequency distribution of extinction intensity, and this distribution, in the form of a "kill curve" for species, shows the expected waiting times between extinction events of a given intensity. The kill curve is an average description of the extinction record and does not imply any cause or causes of extinction.

The kill curve shows, among other things, that only about five percent of total species extinctions in the Phanerozoic were involved in the five largest mass extinctions. The other 95% were distributed among large and small events not normally called mass extinctions.

As an exploration of the possibly absurd proposition that most past extinctions were produced by the effects of large-body impact, the kill curve for species has been mapped on the comparable distribution for comet and asteroid impacts. The result is a curve predicting the species kill for a given size of impacting object (expressed as crater size). The results are reasonable in that impacts producing craters less than 30 km (diameter) cause negligible extinction but those producing craters 100-150 km (diameter) cause extinction of species in the range of 45-60 percent.

GEOGRAPHY OF CRETACEOUS EXTINCTIONS: DATA BASE DEVELOPMENT

D. M. Raup*
University of Chicago

Data bases built from the source literature are plagued by problems of data quality. Unless the data acquisition is done by experts, working slowly, the data base may contain so much "garbage" that true signals and patterns cannot be detected. On the other hand, high quality data bases develop so slowly that satisfactory statistical analysis may never be possible due to the small sample sizes. This report describes results of a test of the opposite strategy: rapid data acquisition by non-experts with minimal control on data quality.

186 published lists of species and genera of fossil invertebrates of latest Cretaceous age (Maestrichtian) were located through a random search of the paleobiological and geological literature. The geographic location for each faunal list was then transformed electronically to Maestrichtian latitude and longitude and the lists were further digested to identify the genera occurring in each ten-degree, latitude-longitude block. The geographical lists were clustered using the Otsuka similarity coefficient and a standard unweight-pair-group method. The resulting clusters are remarkably consistent geographically, indicating that a strong biogeographic signal is visible despite low-quality data.

A further test evaluated the geographic pattern of end-Cretaceous extinctions. All genera in the data base were compared with Sepkoski's compendium of time ranges of genera to determine which of the reported genera survived the Cretaceous mass extinction. In turn, extinction rates for the ten-degree, latitude-longitude blocks were mapped. The resulting distribution is readily interpretable as a robust pattern of the geography of the mass extinction.

The study demonstrates that a low-quality data base, built rapidly, can provide a basis for meaningful analysis of past biotic events.

THE FOSSIL RECORD OF EVOLUTION: DATA ON DIVERSIFICATION AND EXTINCTION

J. J. Sepkoski, Jr.*
University of Chicago

Understanding of the evolution of complex life, and of the roles that changing terrestrial and extraterrestrial environments played in life's history, is dependent upon synthetic knowledge of the fossil record. Paleontologists have been describing fossils for more than two centuries. However, much of this information is dispersed in monographs and journal articles published throughout the world. Over the past several years, I have been surveying this literature and compiling a synoptic data base on times of origination and extinction of fossil genera. The data base, which now holds approximately 32,000 genera, covers all taxonomic groups of marine animals, incorporates the most recent taxonomic assignments, and uses a detailed global time framework that can resolve originations and extinctions to intervals averaging three million years in duration. These data can be used to compile patterns of global biodiversity, measure rates of taxic evolution, and test hypotheses concerning adaptive radiations, mass extinctions, etc. Thus far, considerable effort has been devoted to using the data to test the hypothesis of periodicity of mass extinction.

Rates of extinction measured from the data base have also been used to calibrate models of evolutionary radiations in marine environments. It has been observed that new groups, or "clades," of animals (i. e. orders and classes) tend to reach appreciable diversity first in nearshore environments and then to radiate in more offshore environments; during decline, these clades may disappear from the nearshore while persisting in offshore, deep water habitats. These observations have led to suggestions that there is something special about stressful or perturbed environments that promotes the evolution of novel kinds of animals that can rapidly replace their predecessors. The numerical model that is being investigated to study this phenomenon treats environments along onshore-offshore gradients as if they were discrete habitats. Each habitat contains a set number of genera (as observed in the fossil record). During any time interval, genera within a habitat can become extinct with a probability that varies among clades (as measured from the data base) and increases toward the nearshore (as also observed in the fossil record). Extirpated genera are replaced either by speciation within the habitat or by immigration of genera from adjacent habitats. Solutions of the model demonstrate that extinction-resistant clades will replace extinction-prone clades and that this replacement will proceed along the onshore-offshore gradient regardless of where new clades originate. Thus, patterns of replacement are not dependent on special evolutionary properties of stressed environments. Instead, they reflect radiations of clades whose species are more successful in weathering environmental perturbations. This is the same pattern that is observed in taxonomic selectivity at mass extinctions (including the Cretaceous-Tertiary event): clades that are characterized by low rates of extinction during normal times appear to preferentially survive the abnormal times of mass extinction.

BIOGEOCHEMICAL MODELING AT MASS EXTINCTION BOUNDARIES

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Earth Systems Group, New York University

The causes of major mass extinctions is a subject of considerable interest to those concerned with the history and evolution of life on earth. The primary objectives of the proposed plan of research are: 1) to develop quantitative time-dependent biogeochemical cycle models, coupled with an ocean atmosphere in order to improve our understanding of global scale physical, chemical, and biological processes that control the distribution of elements important for life at times of mass extinctions, and 2) to develop a comprehensive data base of the best available geochemical, isotopic and other relevant geologic data from sections across mass extinction boundaries. These data will be used to constrain and test the biogeochemical model. These modeling experiments should prove useful: 1) in determining the possible cause(s) of the environmental changes seen at bio-event boundaries, 2) in identifying and quantifying little-known feedbacks among the oceans, atmosphere and biosphere, and 3) in providing additional insights into the possible responses of the earth system to perturbations of various timescales.

One of the best known mass extinction events marks the Cretaceous/Tertiary (K/T) boundary (66 Myr ago). Data from the K/T boundary are used here to constrain a newly developed time-dependent biogeochemical cycle model that is designed to study transient behavior of the earth system. Model results predict significant fluctuations in ocean alkalinity, atmospheric CO_2, and global temperatures caused by extinction of calcareous plankton and reduction in the sedimentation rates of pelagic carbonates and organic carbon. Oxygen-isotope and other paleoclimatic data from K/T time provide some evidence that such climatic fluctuations may have occurred, but stabilizing feedbacks may have acted to reduce the ocean alkalinity and carbon dioxide fluctuations.

SESSION VI

SETI

Chairman - J. Tarter

John Billingham (Acting Chief of SETI Office) and Dave Brocker (Project Manager) of Ames Research Center outlined the recent technical and bureaucratic history of NASA's SETI Microwave Observing Project. Together they described how it fit into the overall Exobiology Program and what the Project Management structure was at Ames Research Center (lead center) and the Jet Propulsion Laboratory.

Following this introduction, Larry Webster and Michael Klein (Deputy Project Managers) described the Targeted Search and Sky Survey elements of the Project. Prototype Observing systems are being developed for both elements and software to permit real-time signal detection, and near-time signal recognition is being tested. If funding is forthcoming, these prototypes will be used to inaugurate the MOP observing phase October 12, 1992.

The Targeted Search prototype will provide dual circular polarization, six simultaneous resolutions of 1, 2, 4, 8, 4, 28 Hz covering 10 MHz of input bandwidth and will be capable of detecting drifting and non-drifting CW signals and narrowband pulses. The volume of three dimensional space searched while examining 773 solar-type stars over 1 to 3 GHz is limited by the achieved sensitivity and the unknown transmitter power that determines the effective range for any signal. This prototype will be replicated 6 times to produce the full observational capability of the Targeted Search. Observing systems of 10 MHz bandwidth will be used separately or parallel on large radio astronomy telescopes around the world as well as the DSSN 70 m antennas and a dedicated SETI telescope to complete observations by 1999.

The Sky Survey prototype will initially provide dual circular polarization and a resolution of 20 Hz covering 20 MHz. Software will continuously compare events above threshold as the survey scans the sky and will record for later confirmation those candidates that provide the appropriate point source response along and between the individual scan lines. This prototype will be augmented to provide the full 300 MHz bandwidth coverage and 20 MHz resolution necessary to conduct the Sky Survey search for drifting and non-drifting CW signals. The Sky Survey system will be used on the DSN 34 m antenna at Goldstone (and perhaps also the Madrid station) to search the Northern hemisphere before moving to Tidbinbilla to complete the Sky Survey by 1999.

Stuart Bowyer of UC of Berkeley described the SERENDIP system for commensal SETI observations that has been developed with NASA funds. This system provides a spectrometer with 65,536 channels of 1 Hz resolution and was used to "piggy back" on routine astronomical research programs, primarily at the 300 foot antenna at the NRAO. A significant coverage of "interesting" frequencies and sky directions can thereby be researched without requiring dedicated antenna time. Extensive post-processing is required to remove RFI contamination. About half of the candidate detections from 7000 hours of observation have been re-observed using the 140 foot antenna without re-detection. The SERENDIP system has recently been upgraded and sold to the SETI Microwave Observing Project for its program of RFI studies. These funds will be used to create the next generation of SERENDIP III having 10^8 spectral channels, for continuous deployment at Arecibo on the carriage house counter-balance for the new Gregorian system.

Bob Dixon form the Ohio State University Radio Observatory described the long running SETI Sky Survey program at that site. A number of improvements to this site are possible and could be part of a future upgrade program if funds become available. This site is the only one to continuously monitor its RFI environment with a discone antenna mounted on the main feed horn. In addition, a unique, rapid follow-up search strategy will soon be functioning at the site. Software will make a real-time comparison of events detected above threshold with the expected beam pattern for a point source passing through the dual feed horn system. Whenever a strong event having the correct pattern is detected, the telescope will automatically exit its transit sky survey program and begin to track the detected source across the sky. When the detected source sets, the software will again resume its standard sky survey program. In this way, it is hoped that sufficient data can be collected to recognize the source of detected signals, while they are still present in the antenna field of view.

The last paper of the session by Albert Betz of UC Berkeley described the construction of a high resolution Infrared Spectrometer. This turnable CO_2 laser spectrometer mixes signals down to radio frequencies so that the standard heterodyne techniques can be used to achieve extremely good spectral resolution. It will be used with one of the 1.6 m mirrors from a newly completed IR interferometer to make a 10 µ search of nearby solar-type stars. This search will be the first IR "magic frequency" program. The question of whether signal-to-noise ratio is greater at radio or IR frequencies has been the subject of decades of debate. This question cannot be answered theoretically because it depends on how strongly beamed the transmitted signal is assumed to be (ultimately how extraterrestrial engineers construct large antennas as a function of wavelength!). Like most SETI questions, an experimental solution is the only reasonable approach.

THE NASA SETI PROGRAM

J. Billingham* and D. H. Brocker*
NASA Ames Research Center

In 1959 Morrison and Cocconi proposed that a sensible way to conduct interstellar communication would be to use radio at or near the frequency of hydrogen. In 1960 Frank Drake conducted the first Search for Extraterrestrial Intelligence (SETI) using a radiotelescope at Green Bank in West Virginia. Since 1970 NASA has systematically developed a definitive program to conduct a sophisticated search for evidence of extraterrestrial intelligent life.

The basic hypothesis is that life may be widespread in the universe, and that in many instances extraterrestrial life may have evolved into technological civilizations. The underlying scientific arguments are based on our continuously improving knowledge of astronomy and astrophysics, especially star system formation, and of planetary science, chemical evolution and biological evolution. If only one in a million sun-like stars in our galaxy harbors species with cognitive intelligence, then there are 100,000 civilizations in the Milky Way alone.

The fields of radioastronomy digital electronic engineering, spectrum analysis and signal detection have advanced rapidly in the last twenty years and now allow us to build sophisticated systems to attempt the detection of ETI signals. In concert with the scientific and engineering communities NASA has developed, over the last several years, a Microwave Observing Project whose goal is to design, build and operate SETI systems during the decade of the nineties in pursuit of the goal of signal detection. The Microwave Observing Project is now approved and underway. It is managed in Washington as a part of the Exobiology Program in the Division of Life Sciences at NASA HQ. It is supported with additional funding from the Office of Space Operations. Ames and JPL carry out the Project, with Ames as Lead Center. There are two major components in the Project, the Targeted Search Element, under Ames management, and the Sky Survey Element, under JPL management. The total budget for the Microwave Observing Project is $115 over the ten year period 1990-1999. More detailed descriptions of the two elements of the Project are given in the following reports by the Ames and JPL Project Managers, respectively.

NASA-SETI MICROWAVE OBSERVING PROJECT - TARGETED SEARCH ELEMENT

L. D. Webster*
NASA Ames Research Center

The Targeted Search Element (TSE) performs one of two complimentary search strategies of the NASA-SETI Microwave Observing Project (MOP): the Targeted Search. The principle objective of the Targeted Search strategy is to scan the microwave window between the frequencies of one to three gigahertz for narrow-band microwave emissions eminating from the direction of 773 specifically targeted stars. The scanning process is accomplished at a minimum resolution of one or two Hertz at very high sensitivity. Detectable signals will be of a continuous wave or pulsed form and may also drift in frequency. The TSE will possess extensive Radio Frequency Interference (RFI) mitigatation and verification capability as the majority of signals detected by the TSE will be of local origin. Any signal passing through RFI classification and classifiable as an Extraterrestrial Intelligence (ETI) candidate will be further validated at non-MOP observatories using established protocol.

The Targeted Search will be conducted using the capability provided by the Targeted Search Element. The TSE provides six Targeted Search Systems (TSS) which independently or cooperatively perform automated collection, analysis, storage, and archive of signal data. Data is collected in 10 megahertz "chunks" and signal processing is performed at a rate of of 160 megabits per second. Signal data is obtained utilizing the largest radio telescopes available for the Targeted Search such as those at Arecibo and Nancay or at the dedicated NASA-SETI facility. This latter facility will allow continuous collection of data. The TSE also provides for TSS utilization planning, logistics, remote operation, and for off-line data analysis, and permanent archive of both the Targeted Search and Sky Survey data.

The TSE is being developed "in-house" by the NASA Ames Research Center (ARC). ARC is performing TSE Systems Engineering and developing a preproduction version of the Targeted Search System (TSS). The preproduction TSS will be used to initiate the MOP Targeted Search on Columbus Day, 1992 at the Arecibo Observatory in Puerto Rico.

NASA SETI MICROWAVE OBSERVING PROJECT - SKY SURVEY ELEMENT

M. J. Klein*
Jet Propulsion Laboratory, California Institute of Technology

The SETI Sky Survey observing program is one of two complimentary strategies that NASA plans to use in its microwave Search for Extraterrestrial Intelligence (SETI). The primary objective of the Sky Survey is to search the entire sky over the frequency range 1.0 GHz to 10.0 GHz for evidence of narrow band signals of extraterrestrial, intelligent origin. Frequency resolutions of 30 Hz or narrower will be used across the entire band. Spectrum analyzers with upwards of ten million channels are required to keep the survey time approximately 6 years. Data rates in excess of 10 megabits per second will be generated in the data taking process. Sophisticated data processing techniques will be required to determine the ever changing receiver baselines, and to detect and archive potential SETI signals. Existing radio telescopes, including several of NASA's Deep Space Network (DSN) 34 meter antennas located at Goldstone, CA., and Tidbinbilla, Australia, will be used for the observations. The Jet Propulsion Laboratory has the primary responsibility to develop and carry out the Sky Survey.

In order to lay the foundation for the full scale SETI Sky Survey, a prototype system is being developed at the Jet Propulsion Laboratory. The system will be installed at the new 34-m high efficiency antenna at the DSS 13 research and development station, Goldstone, CA, where it will be used to initiate the observational phase of the NASA SETI Sky Survey. It is anticipated that the early observations be useful to test signal detection algorithms, scan strategies, and RFI rejection schemes. The "SETI specific" elements of the prototype system are:

(a) the Wide Band Spectrum Analyzer (WBSA); a 2-million channel FFT spectrum analyzer which covers an instantaneous bandpass of 40 MHz.
(b) the signal detection processor: a hardware module which executes a detection algorithm "along the scan", which reduces the data rate by factors of 1,000 or more.
(c) the SETI Sky Survey Manager, a network-based C-language environment that provides observatory control, performs data acquisition and analysis algorithms.

A high level description of the prototype hardware and software systems will be given and the current status of the system development will be reported.

This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

THE SERENDIP II SETI PROJECT: CURRENT STATUS

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and M. Lampton
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Over the past 30 years interest in extraterrestrial intelligence has progressed from philosophical discussion to rigorous scientific endeavors attempting to make contact. Since it is impossible to assess the probability of success and the amount of telescope time needed for detection, SETI projects are plagued with the problem of attaining the large amounts of time needed on the world's precious few large radio telescopes. To circumvent this problem, the SERENDIP instrument operates autonomously in a piggyback mode utilizing whatever observing plan is chosen by the primary observer. In this way large quantities of high-quality data can be collected in a cost-effective and unobtrusive manner.

During normal operations, SERENDIP logs statistically significant events for further off-line analysis. Due to the large number of terrestrial and near-space transmitters on earth, a major element of the SERENDIP project involves identifying and rejecting spurious signals from these sources. Another major element of the SERENDIP project (as well as most other SETI efforts) is detecting ETI signals. Events selected as candidate ETI signals are studied further in a targeted search program which utilizes between 24 to 48 hours of dedicated telescope time each year.

REOPTIMIZATION OF THE OHIO STATE UNIVERSITY RADIO TELESCOPE FOR THE NASA SETI PROGRAM

R. S. Dixon
The Ohio State University Radio Observatory

The Ohio State University radiotelescope is the second largest radio telescope in the United States, equivalent in collecting area (2200 m^2) to a 175-foot diameter dish. For the past 17 years it has been dedicated fulltime to SETI, and it is now being considered by NASA for selection as the NASA dedicated SETI observatory.

The telescope was originally designed, optimized, and used as an all-sky survey instrument to create detailed maps and catalogs of the radio astronomical sky. For the SETI program, some reoptimizations are required.

Right ascension tracking for one to two hours (depending on the declination) has been achieved by exploiting the exceptionally large f/d ratio of the telescope. The feed horns have been mounted on a large moveable, rubber-tired cart which is capable of a total motion of 100 feet. The cart can carry many horns, making possible simultaneous observations at many sky directions and frequency ranges.

Rapid declination movement and its automation will be accomplished through simplification of the existing braking system, and replacement of older mechanical sensors by modern electronic inclinometers and proximity detectors.

Circular polarization capability will be achieved through an increase in the number of horizontal wires in the reflector mesh, or addition of a finer mesh on top of the existing one.

The telescope has great inherent resistance to radio frequency interference, due to its ground-mounted feed horns and shielding by the large reflectors of half the horizon. The resistance has been recently increased further by installation of rolled-edges and diffraction-trapping gratings on the feed horns. If further shielding should be required, inexpensive side shields could be added to the telescope, making it a totally closed structure on all four sides.

A DIRECTED SEARCH FOR EXTRATERRESTRIAL LASER SIGNALS

A. Betz
Space Sciences Laboratory

The focus of NASA's SETI program is on microwave frequencies, where receivers have the best sensitivities for the detection of narrowband signals. Such receivers, when coupled to existing radio telescopes, form an optimal system for broad area searches over the sky. For a *directed* search, however, such as toward specific stars, calculations show that infrared wavelengths can be equally as effective as radio wavelengths for establishing an interstellar communication link. This is true because infrared telescopes have higher directivities (gains) that effectively compensate for the lower sensitivities of infrared receivers. The result is that, for a given level of transmitted power, the S/N ratio for communications is equally as good at infrared and radio wavelengths. It should also be noted that the overall sensitivities of both receiver systems are quite close to their respective fundamental limits: background thermal noise for the radio frequency system and quantum noise for the infrared receiver. Consequently, the choice of an optimum communication frequency may well be determined more by the achievable power levels of transmitters rather than the ultimate sensitivities of receivers at any specific frequency. In the infrared, CO_2 laser transmitters with power levels >1 MW can already be built on Earth. For a slightly more advanced civilization, a similar but enormously more powerful laser may be possible using a planetary atmosphere rich in CO_2. Because of these possibilities and our own ignorance of what is really the "optimum" search frequency, a search for narrowband signals at infrared frequencies should be a part of a balanced SETI program.

Detection of narrowband infrared signals is best done with a heterodyne receiver functionally identical to a microwave spectral line receiver. We have built such a receiver for the detection of CO_2 laser radiation at wavelengths near 10 μm (30 THz). The spectrometer uses a high-speed HgCdTe diode as the photomixer and a small CO_2 laser as the local oscillator. Output signals in the intermediate frequency range 0.1-2.6 GHz are processed by a 1000-channel acousto-optic (AOS) signal processor. The receiver is being used on a 1.5-m telescope on Mt. Wilson to survey a selected sample of 150 nearby stars. The current status of the work will be discussed along with a prognosis for further technical development and observational work.

SESSION VII

SOLAR SYSTEM EXPLORATION (II)

Chairman - G. C. Carle

The concluding session of the Symposium was comprised of a spectrum of presentations related to the extraterrestrial aspects of exobiology. Subjects ranged from planetary protection to instrumentation for the exploration of Titan, and from advanced technology development for future missions to the importance of meteors and comets to prebiotic chemistry.

D. DeVincenzi began the session with a report on planetary protection in respect to the Space Exploration Initiative announced last year by U.S. President Bush. The central focus of the Initiative is to establish a manned presence on Mars which will require a number of robotic precursor missions. With each of these missions, cross contamination of Earth and Mars becomes an important issue. To address questions related to this issue, a workshop was held, the preliminary result of which was a report which made several recommendations for dealing with forward and backward contamination as well as non-scientific issues including public relations, legal, regulatory, international, and environmental concerns. The report will be further discussed when it is presented at the next COSPAR meeting.

The next paper was presented by W. Irvine who discussed an analysis of the images of Phobos obtained from the recent Soviet mission to the martian system with the Phobos 2 spacecraft. Earlier ground-based and flight data indicates that Phobos may be a captured C-type asteroid which could contain relatively unaltered organic as well as preserved interstellar material representative of the early history of the solar system. Unfortunately, both Phobos 1 and 2 suffered major technical failures and only a small number of images were obtained by the FREGAT camera. Results-to-date include root-mean-square surface slopes, albedo fluctuations, and corresponding correlation lengths.

G. Carle presented a paper describing an instrument he and his colleagues have proposed for the Cassini Mission. The Cassini Mission is a joint undertaking of the National Aeronautics and Space Administration and the European Space Agency to explore the saturian system with a Saturn orbiter and the Huygens Probe (a Titan atmospheric entry probe). The mission will be launched in 1996 and arrive at Titan in 2003. The proposed instrument is the Titan Aerosol and Gas Experiment (TAGEX) which, if selected, will identify and quantify the major and trace components of the atmospheric aerosols and gases. Such measurements would aid in the understanding of planetary-scale organic chemistry and help clarify prebiotic processes on Titan as well as on Earth.

D. Kojiro followed with a paper describing the use of an advanced ion mobility spectrometer to analyze model components of Titan's atmosphere. The instrument described will be a fundamental part of TAGEX if it is selected. The ion mobility spectrometer is an atmospheric pressure, chemical detector that quantifies and produces an identifying spectrum for each chemical species analyzed. Conventional ion mobility spectrometers use a molecule-ion reaction based on water to ionize each analyte, which is not appropriate for hydrocarbons. The newly developed instrument uses either an ultra-dry system or metastable ionization to accomplish ionization, thus extending the capability to the hydrocarbons and increasing sensitivity by several orders of magnitude.

T. Shen presented work he has conducted in developing novel and powerful gas chromatograph columns that can be used with the advanced detectors required for flight experiments. These columns are based on a new silicone polymer developed by him and can rapidly and efficiently separate mixtures of highly polar compounds, such as amines, and nonpolar organics, such as hydrocarbons. He also presented preliminary results from a mathematical model which is being developed to predict the chromatographic behavior of potential polymeric structures before they are synthesized.

J. Valentin presented the results of studies on various advanced gas chromatographic analytical concepts for possible use in future planetary missions. He reported on the first-time use of Multiplex Gas Chromatography for samples which changed in composition and concentration during the analytical sampling period, and a water-specific instrument based on this technique which is under development for a future Mars mission. Another area reported upon was the technique of cryofocussing which provides the capability to collect samples from low pressure environments for very low level (ppb) analysis; this technique has been included the TAGEX instrument which was proposed for the Cassini-Huygens Probe mission.

The last paper of the session was presented by S. Miller who reported on theoretical considerations of the fate of prebiotic amino acids including those supplied from extraterrestrial sources and those produced in the primitive atmosphere. It was reasoned that amino acids cannot accumulate over more than 10^7 years because the entire ocean cycles through hydrothermal vents during this time period thus any accumulated amino acids would be destroyed. It was further estimated that during this period atmospheric processes would produce an amino acid concentration of $\approx 10^{-4}$ M in an ocean of present size. Further, it was concluded that cometary and meteoritic contributions to the prebiotic earth were only a few percent of the Earth-based synthesis.

PLANETARY PROTECTION ISSUES AND HUMAN EXPLORATION OF MARS

D. L. DeVincenzi
NASA Ames Research Center

A key feature of the Space Exploration Initiative announced last year by the President involves human missions to Mars. The report describing the initiative cites the search for life on Mars, extant or extinct, as one of five science themes for such an endeavor. Because of this, concerns for Planetary Protection (PP) have arisen on two fronts: 1) forward contamination of Mars by spacecraft-borne terrestrial microbes which could interfere with exobiological analyses, and 2) back contamination of Earth by species that may be present in returned Mars samples. The US is also signatory to an international treaty designed to protect Earth and planets from harmful cross-contamination during exploration. Therefore, it is timely to assess the necessity for, and impact of, PP procedures on the mission set comprising the human exploration of Mars.

A recent Workshop addressed PP questions of this type. The following ground-rules were adopted: 1)information needed for PP must be obtained during the robotic precursor phase prior to human landings, 2) returned samples will be considered biologically hazardous until proven otherwise, 3) deposition of microbes on Mars is inevitable when humans land, and 4) human landings are unlikely until it is demonstrated that there is no harmful effect of martian materials. These considerations drove the adoption of a conservative PP strategy for precursor missions as follows: 1) for forward contamination prevention, all orbiters will have Mars Observer-like controls on assembly, trajectory, and lifetime. All landers will have Viking-like controls on assembly, sterilization, and bioshield, and 2) for back contamination prevention, all sample return missions will have controls including hardware sterilization, bioshield, fail-safe sample sealing, break contact chain with surface, and Earth containment and quarantine analysis. In addition, the Workshop produced several recommendations for dealing with forward and back contamination concerns from non-scientific perspectives, including public relations, legal, regulatory, international, and environmental.

ANALYSIS OF IMAGES OBTAINED BY THE PHOBOS 2 SPACECRAFT

W. M. Irvine*
University of Massachusetts

The reflection spectrum and density of the Martian satellite Phobos suggest that it may be a captured C-type asteroid and hence may contain relatively unaltered organic material from the early history of the solar system. Since there is evidence from the isotopic anomalies that meteorites presumably derived from such asteroids contain preserved interstellar material, it is conceivable that evidence for interstellar matter might also be present on Phobos. The present research concerns interpretation of the chemical composition of Phobos' surface and analysis of images of Phobos taken by the FREGAT camera equipment aboard the Phobos 2 spacecraft, including both disk-integrated and disk-resolved photometry. Because the surface of Phobos is a regolith (a pulverized surface layer of irregular texture), spectral information on the surface composition will be convolved with information on the surface texture. A primary goal of the present research has been to untangle these effects.

Unfortunately, the spacecraft Phobos 1 lost contact with Earth during its transit to Mars, and Phobos 2 likewise lost contact after two months in orbit around Mars. Thus, the "hovering" phase of very close approach and the landing of instruments on the surface of Phobos did not take place, so that no data on the elemental composition of the surface is available. However, thirty-seven images were obtained of the satellite. The results include the first such observations at near infrared wavelengths, for which disk-integrated results show that the corresponding geometric albedo is quite small and very similar to the value in the blue. The resolved surface photometry has been analyzed by developing new methods of radiative transfer in rough surface layers and a procedure referred to as "statistical photoclinometry". The results provide rms surface slopes on scales from the order of 1 millimeter to 250 meters, albedo fluctuations, and corresponding correlation lengths.

TITAN AEROSOL AND GAS EXPERIMENT FOR THE HUYGENS PROBE

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The Cassini mission is a joint undertaking of the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) to explore the Saturnian system with a Saturn orbiter and a Titan probe. The launch vehicle and the Saturn orbiter are the responsibility of NASA while the Huygens Probe (the detachable Titan probe) is the responsibility of ESA. The spacecraft will be launched in 1996 and the Huygens Probe will arrive at Titan in 2003.

The Cassini Mission - Huygens Probe provides a unique opportunity to obtain detailed information about the atmosphere and, possibly, the surface of Titan. Titan possesses a substantial nitrogen atmosphere containing methane and many other organic compounds. Although the conditions on present day Titan are significantly different from the primitive Earth, Titan provides a venue for both comparative planetology and the study of certain aspects of exobiology on a planetary scale. For example, within Titan's atmosphere, irreversible conversion of methane, presumably dominated by photochemical reactions, into more complicated models which settle to and remain on the surface is taking place. Aerosols play an important role in the atmospheric processes on Titan. An understanding of these processes will help clarify prebiotic chemical and physical processes not only on Titan, but also on primitive Earth. The Huygens probe offers an opportunity to determine how organic particles are formed and grow which will, again, clarify their role on the early Earth.

A powerful analytical instrument, capable of addressing the above exobiology and other science questions, was recently proposed by the authors for the Huygens Probe. It is comprised of an aerosol and gas sampler and processor and a gas chromatograph - ion mobility spectrometer. The instrument will be able to measure complex organics that make up the collected aerosols to the ~1 ppm level. Gases will be measured to the ~10 ppb. Because the Titan atmosphere is expected to be quite complex, a gas chromatograph - ion mobility spectrometer is used to provide unequivocal identification of the components of the analytes.

Further details of the science questions to be investigated will be discussed and the proposed instrument will be described. Expected results and their implications will also be addressed.

ANALYSIS OF MODEL TITAN ATMOSPHERIC COMPONENTS USING ION MOBILITY SPECTROMETRY

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and
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A detailed knowledge of the history and abundances of the biogenic elements and their compounds throughout the solar system can provide exobiologists with a basis for understanding the conditions necessary for chemical evolution and the origin of life. Flight experiments conducting *in situ* analyses have already produced a wealth of information on the environments of Venus and Mars. Future missions will require instrumentation capable of providing identification and quantitation of a multitude of molecular species over a wide range of concentrations. As one of these future missions, NASA, in conjunction with the European Space Agency, plans to send a spacecraft to the Saturnian system (Cassini mission) to study Saturn and its satellite, Titan. An analysis of Titan's atmosphere presents a highly challenging task because of the complexity of the analysis, particularly in terms of the many species of organic carbon compounds that may be present, and the very low concentration levels that must be detected. The Gas Chromatograph - Ion Mobility Spectrometer (GC-IMS) has been proposed as an analytical technique for the analysis of Titan's atmosphere.

The Ion Mobility Spectrometer (IMS) is an atmospheric pressure, chemical detector that produces an identifying spectrum of each chemical species measured. When the IMS is combined with a Gas Chromatograph (GC) as a GC-IMS, the GC is used to separate the sample into its individual components, or perhaps small groups of components. The IMS is then used to detect, quantify, and identify each sample component. Conventional IMS detection and identification of sample components depends upon a source of energetic radiation, such as beta radiation, which ionizes the atmospheric pressure host gas. This primary ionization initiates a sequence of ion-molecule reactions leading to the formation of sufficiently energetic positive or negative ions, which in turn ionize most constituents in the sample. In conventional IMS, this reaction sequence is dominated by the water cluster ion. However, many of the light hydrocarbons expected in Titan's atmosphere cannot be analyzed by IMS using this mechanism at the concentrations expected. Research at NASA Ames and PCP Inc., has demonstrated IMS analysis of expected Titan atmospheric components, including saturated aliphatic hydrocarbons, using two alternate sample ionizations mechanisms. The sensitivity of the IMS to hydrocarbons such as propane and butane was increased by several orders of magnitude. Both ultra dry (waterless) IMS sample ionization and metastable ionization have successfully been used to analyze a model Titan atmospheric gas mixture.

A SILICONE COLUMN FOR GC ANALYSIS OF POLAR AND NONPOLAR CHEMICALS

T. C. Shen*
SETI Institute, NASA Ames Research Center

The investigation of the Saturnian system is being proposed jointly by NASA and ESA. The mission is scheduled for a launch in 1996. The mission provides an opportunity for close observation and exploration of Saturn's atmosphere, the complex Saturnian system of satellites and rings, Titan (Saturn's planet-sized moon), and Saturn's magnetosphere. The mission gives special attention to Titan which is blanketed by a thick. opaque atmosphere. An atmospheric probe will be deposited into the Titan atmosphere for *in situ* measurement during a slow, three hours descent to the surface. The results from this analysis may provide the information which is important to the research of chemical evolution, and the origin of life.

We have developed an analytical system as a part of the Titan Aerosol Gas Experiment (TAGEX), a proposed experiment for the Cassini mission. This system will use two highly sensitive detectors, MID (metastable ionization detector) and IMS (ion mobility spectrometer). Unfortunately, when commercial columns are utilized with these highly sensitive detectors, volatile components continuously bleed from the column and interfere with the detector. In addition, light columns must be able to separate polar and nonpolar organic chemicals within 10-15 minutes under isothermal conditions for the Titan mission. Therefore, we have developed a highly crosslinked silicone polymeric packed column which is able to efficiently separate amines, alcohols, and hydrocarbons with retention times less than 15 minutes at 100°C isothermal condition.

GAS CHROMATOGRAPHIC CONCEPTS FOR THE ANALYSIS OF PLANETARY ATMOSPHERES

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Over the last few years, new GC concepts have been developed for use on board spacecraft or any other restricted environments for determining the chemical composition of the atmosphere and surface material of various planetary bodies. Future NASA missions include an entry probe that will be sent to Titan and various spacecraft that will land on Mars. In order to be able to properly respond to the mission science requirements and physical restrictions imposed on the instruments by these missions, GC analytical techniques are being developed in our Branch. Some of these techniques include hardware and mathematical techniques that will improve GC sensitivity and increase the sampling rate of a GC descending through a planetary atmosphere.

The technique of Multiplex Gas Chromatography (MGC) is an example of a technique that was studied in a simulated Titan atmosphere. In such an environment that atmospheric pressure at instrument deployment is estimated to be a few torr. Thus, at such pressures the small amount of sample that will be acquired might not be enough to satisfy the detection requirements of the gas chromatograph. In MGC many samples are pseudo-randomly introduced to the chromatograph without regard to elution of preceding components. The resulting data is then reduced using mathematical techniques such as cross-correlation or Fourier Transforms. Advantages realized from this technique include: improvement in detection limits of several orders of magnitude and increase in the number of analyses that can be conducted in a given period of time.

Results proving the application of MGC at very low pressures emulating the same atmospheric pressures that a Titan probe will encountered when the instruments are deployed will be shown. The sample used contained hydrocarbons that are expected to be found in Titan's atmosphere. In addition, a new selective modulator was developed to monitor water under Martian atmospheric conditions. Since this modulator is selective only to water, the need for a GC column is eliminated. This results in further simplification of the instrument.

THE RELATIVE IMPORTANCE OF PREBIOTIC SYNTHESIS ON THE EARTH AND INPUT FROM COMETS AND METEORITES

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We have been studying the prebiotic synthesis of hydrogen cyanide and formaldehyde by the action of electric discharges on various model primitive atmospheres containing CH_4, CO and CO_2. Photochemical production rates would also have been important and have been calculated for HCN and H_2CO. A reasonable rate of synthesis of amino acids from these sources is about 10 n moles $cm^{-2}yr^{-1}$ or 0.10 moles cm^{-2} in 10^7 yrs. This would give a concentration of 3×10^{-4} M in an ocean of the present size (300 liters cm^{-2}). The amino acids cannot accumulate over a longer period because the entire ocean passes through the 350°C submarine vents in 10^7 yrs, which decomposes all the organic compounds.

A number of workers have calculated the influx of comets and meteorites on the primitive earth, both as a destructive process for organic compounds and for any life that was present, as well as a source of organic compounds. Some of the amino acids from the meteorite proposed to have hit the earth 65×10^6 yrs ago have been detected at the Cretaceous/Tertiary boundary sediments.

The problem with proposing a large scale input of organic compounds from meteorites and comets is that they must survive passage through the atmosphere and impact. There are some processes that would allow survival such as showers of centimeter to meter sized meteorites and various aerodynamic braking processes for larger objects. Even if a significant amount of the organic material survived impact, the destructive processes in the hydrothermal vents would remove these compounds on the average in 10^7 yrs or less. If it is assumed that the input rate was sufficient to overcome these destructive processes, then too much carbon and water, especially from comets, would have been added to the surface of the earth. We conclude that while some organic material was added to the earth from comets and meteorites, the amount available from these sources at a given time was only a few percent of that from earth based syntheses.

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Poster Session

"LIFE ON ICE, ANTARCTICA AND MARS"

D. T. Andersen
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> "Within our solar system, there are two worlds where rock and ice and chilling winds rule bleak landscapes. Once both were warmer, and rivers wandered through valleys where today the highest temperatures just barely pass the melting point of liquid water. In one of them winter lasts four months of freezing darkness. Upon the other, winter has lasted three billion years or more. Two lands where life had a chance to flourish. Two lands where - at first - it seems no trace of life remains. But one of them is rich in hidden life, though alien and strange. And the other is a planet we yearn to explore with the wisdom gained from discoveries. This is the story of Antarctica and Mars, a courageous and astonishing search for life that has taken humans deep below the icy crust of lakes near Earth's south pole, and given us tools to search for ancient life on the planet Mars."
>
> *From LIFE ON ICE, ANTARCTICA AND MARS*

The study of the origin of life and the prospects for human exploration of Mars are two themes developed in a new 57-minute film, **Life on Ice, Antarctica and Mars**, produced by the InnerSpace Foundation and WHRO Television for broadcast by PBS. What follows is a brief explanation of the film and how it relates to the future human exploration of space.

The film is about exploration in the traditional sense - Antarctica, diving, living in tents, adventure, risk - and in a not-so-traditional sense - the rationale for sending people to the planet Mars. This film relates directly to the Space Exploration Initiative now under study by NASA and the National Space Council. It educates the viewer about the planet Mars and helps explain the need for pursuing such an initiative, while conveying its inherent excitement. The story line is easy to follow, the photography is spectacular, and the narration is excellent.

"Life on Ice" is also about the study of microbial life forms thriving on the bottom of perpetually ice-covered (up to 18 feet thick) lakes in the dry valleys of Antarctica. The research team featured in the film includes exobiologists Dale Andersen (now with Lockheed Engineering & Sciences Co, in support of the Life Sciences Division at NASA Headquarters); planetary scientist Christopher P. McKay of NASA's Ames Research Center; exobiologist Robert Wharton of the Desert Research Institute in Reno, Nevada (at NASA Headquarters for 1989-91 under the Visiting Senior Scientist program); biologist George Simmons of the faculty of Virginia Tech; planetary geologist Steve Squyres of Cornell University; John D. Rummel, the Exobiology Program Manager for the Life Sciences Division, NASA Headquarters; and Carl Sagan, David Duncan Professor of Astronomy and Space Sciences, and Director of the Laboratory for Planetary Studies at Cornell University.

The film, written by Geoff Haines-Styles and produced by Mark Jenkins, relates Antarctic research to the study of the origins of life and to the question of whether life ever existed on Mars (or anywhere else beyond Earth). The film also shows how the working experience gained by this research team relates to planning for human missions to Mars or other harsh, isolated environments.

IDENTIFICATION AND CHARACTERIZATION OF EXTRATERRESTRIAL NON-CHONDRITIC INTERPLANETARY DUST

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Interplanetary Dust Particles (IDPs) are among the most pristine and primitive extraterrestrial materials available for direct study. Most of the stratospheric particles selected for study from the JSC Curatorial Collection have been chondritic in composition (major element abundances within a factor of two of chondritic meteorites) because of this composition virtually ensures that the particle is from an extraterrestrial source.

It is likely that some of the most interesting classes of IDPs have not been recognized simply because they are not chondritic or do not fit established criteria for extraterrestrial origin. Indeed; mass spectroscopy data from the Giotto flyby of comet Halley indicate that a substantial fraction of the dust is in the sub-micron size range and that a majority of these particles contain C,H,O, and/or N as major elements.

The preponderance of CHON particles in the coma of Halley implies that similar particles may exist in the JSC stratospheric dust collection. However, the JSC collection also contains a variety of stratospheric contaminants from terrestrial sources which have these same characteristics. Because established criteria for extraterrestrial origin may not apply to such particles in individual cases, an integrated approach is required in which a variety of analysis techniques is applied to the same particle.

Non-chondritic IDPs, like their chondritic counterparts, can be used to elucidate pre- and early solar system processes and conditions. The study of non-chondritic IDPs may additionally yield unique information which bears on the nature of cometary bodies and the processing of carbonaceous and other low atomic number materials.

We will utilize a suite of complementary techniques, including Low Voltage Scanning Electron Microscopy (LVSEM), Energy-Dispersive X-ray Microanalysis (EDX), Secondary Ion Mass Spectrometry (SIMS) isotope-ratio imaging and Analytical Electron Microscopy (AEM) to accomplish the following two objectives: 1. Develop criteria for the unequivocal identification of extraterrestrial non-chondritic IDPs, and 2. Infer IDP parent body, solar nebula and pre-solar conditions through the study of phases, textures and components contained within non-chondritic IDPs. The general approach we are taking is designed to maximize the total information obtained from each particle. Techniques will be applied in order from least destructive to most destructive.

LVSEM is the premier technique for the high resolution non-destructive surface imaging of particles. The powerful combination of LVSEM with Secondary Ion Mass Spectroscopy (SIMS) isotope ratio imaging allows for the first time the identification of isotopic hot spots and their correlation with original phases and/or morphological features within intact particles.

The application of SIMS isotope ratio imaging to ultramicrotome thin sections of particles allows for the first time the complete characterization by Analytical Electron Microscopy (AEM) of phases which harbor isotopic anomalies.

The result of this investigation will be a data set on a variety of non-chondritic IDPs including surface morphology, bulk composition, D/H isotopic ratios and nanometer-scale phase identification using AEM.

From these date we anticipate that objective criteria can be established for the extraterrestrial and/or interstellar origin(s) of non-chondritic carbonaceous IDPs. Using known stability relationships, phase equilibria and the like, it should be possible to constrain interstellar, pre- and early solar system condition extant during formation and aggregation of the parent bodies represented by the IDPs.

LDEF POST-RETRIEVAL EVALUATION OF EXOBIOLOGY INTERESTS

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Diafin

Cursory examination of LDEF (Long Duration Exposure Facility) shows the existence of thousands of impact craters of which less than 1/3 exceed 0.3 mm in diameter; the largest crater is 5.5 mm. Few craters show oblique impact morphology (low impact angle) and, surprisingly, only a low number of craters have recognizable impact debris (ejecta spray patterns, crater interior impactor residue). Study of this debris could be of interest to Exobiology in terms of C content and carbonaceous materials. All craters > 0.3 mm have been imaged and recorded into a data base by the preliminary examination team (the "A-Team"). Various portions of LDEF surfaces are contaminated by outgassed materials from experimenters trays, in addition to LDEF autocontamination and impact with orbital debris not of extraterrestrial origin.

Because IDPs (interplanetary dust particles, a.k.a. cosmic dust) nominally impacted LDEF at velocities > 3 km/s, the potential for intact survival of carbonaceous compounds is mostly unknown for hypervelocity impacts. Calculations show that for solid phthalic acid (a test impactor), molecular dissociation would not necessarily occur below 3 km/s, if all of the impact energy was directed at breaking molecular bonds, which is not the case (e.g., most energy is used for crater formation and impactor fragmentation). We performed hypervelocity impact experiments (LDEF analogs) by using the Ames Vertical Gun Facility. Grains of phthalic acid and the Murchison meteorite (grain dia.= 0.2 mm for both) were fired into Al plate at 2.1 and 4.1 km/s, respectively. Laser ionization mass spectrometry (LIMS) microanalyses of the impactor residues confirm that phthalic acid molecules remain intact on impact at 2.1 km/s and some of the carbonaceous compounds in Murchison retain their molecular integrity on impact at 4.1 km/s. We assume that some of the LDEF craters were formed at impact velocities < 5 km/s and conclude that meaningful biogenic elemental and compound information can be obtained from IDP impacts on LDEF.

An LDEF catalog of preliminary observational data and imagery will be made available within the 1991 fiscal year (Johnson Space Center, NASA). Sample analysis opportunities will also be announced in the near future through the LDEF Project Office (Langley Research Center, NASA).

RECENT SPECTROSCOPIC FINDINGS CONCERNING CLAY/WATER INTERACTIONS AT LOW HUMIDITY: POSSIBLE APPLICATIONS TO MODELS OF MARTIAN SURFACE REACTIVITY

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and
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The Viking expedition to Mars provided an invaluable, but still little appreciated lesson for die-hard Vitalists among the scientific community and public at large. Not every chemical sequence of cosmochemical evolutionary significance is mediated by "living cells," even those with cosmochemical ramifications for the generation and maintenance of complex life forms. Egotists that we all are, life forms are interesting to us in how they produce their chemistry and in what they can achieve using it. However, cells are by no means unique in the chemistry that they can produce. Viking performed four chemical tests for cellular life forms; Mars passed all but the requirement for significant quantities of organic carbon. Mineral surfaces proved capable of most, if not all, of the chemistry formerly tagged as diagnostic of cellular life. Whereas we now reluctantly acknowledge the chemical facility of mineral systems, we still understand it only primitively. Nor do we even know the surface mineralogy of our closest planetary neighbors. Mineralogists and space scientists, while cognizant of the centrality of planetary mineralogy in planetary formation and evolution, have yet to fully credit the actuality that, among mineral types consistent with the Viking elemental analysis, some are more interesting than others on the basis of their capacity to drive surface chemistry of types producing precursors and constituents of cellular life. Among those minerals "more equal" to Exobiologists are the phyllosilicates, carbonates and phosphates that are postulated or known to be catalysts of biologically interesting organic chemistry, or to be relics of cellular life forms. Analysis of Viking elemental data and surface chemical simulations allow consideration of variably iron cation-exchanged montmorillonites as plausible MarSAMs. Analysis of Martian surface reflectance data are more inclusive than, even at odds with this simple model. However, quantitatively estimated mineralogy using reflectance data is a risky business in the light of our abysmally developed repository of ground based truth regarding structurally defective, non-stoichiometric materials and mineral mixtures in the less than 2µ particle size range.

We have extended a feasibility study assessing the utility of our adaptation of near infrared correlation spectroscopy to quantifying iron and adsorbed water in some clay-based MarSAMs. The work was intended to constitute Phase I of a novel approach to identifying optical analytical wavelength regions, not only for important mineral classes, but for chemically active centers within them. Many of these centers are common to unrelated mineral classes and of disproportionate influence relative to the mineral structure as a whole in determining the surface reactivity of mineral surfaces. We previously reported linearity between reflectance and total iron and total moisture over a large range of both key variables. We also discovered interesting relationships between the intensity of iron bands and the relative humidity of the systems. These relationships now have been confirmed. We show also that, in the low humidity range, reflectance is linearly dependent on a different kind of water from that best representing the full humidity range (the kind of water associated, in clays, with surface acidity). These relationships and the sensitivity and capability of quantitation of NIR data indicate high promise of the method for being able to predictively correlate mineral spectroscopy with the production of reactive surface intermediates or products of surface reactions.

CRYSTAL-FIELD-DRIVEN REDOX REACTIONS: HOW COMMON MINERALS SPLIT H_2O AND CO_2 INTO REDUCED H_2 AND C PLUS OXYGEN

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It is difficult to prove the presence of molecular H_2 and reduced C in minerals containing dissolved H_2 and CO_2. We developed a new technique by which we can unambiguously show that minerals grown in viciously reducing environments contain peroxy in their crystal structures. These peroxy represent interstitial oxygen atoms left behind when the solute H_2O and/or CO_2 split off H_2 and C as a result of internal redox reactions, driven by the crystal field. The observation of peroxy affirms the presence of H_2 and reduced C. It shows that the solid state is indeed an unusual reaction medium.

KINETICS OF THE TEMPLATE-DIRECTED OLIGOMERIZATION OF GUANOSINE 5'-PHOSPHATE-2-METHYLIMIDAZOLIDE: EFFECT OF TEMPERATURE ON INDIVIDUAL STEPS OF REACTION

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Non-enzymatic, template-directed reactions have been proposed as models for prebiological polynucleotide synthesis (Orgel, 1986). Chemically activated mononucleotides react in the presence of a polynucleotide, acting as the template in a Watson-Crick base-pairing fashion, and form the complementary daughter-polynucleotide. Phosphoimidazolide-activated nucleotides have been used successfully as substrates in these reactions (Inoue and Orgel, 1983).

We studied the kinetics of the guanosine 5'-monophosphate-2-methylimidazolide (2-MeImpG) reaction in aqueous pH 8.0 solutions in the presence and in the absence of polycytidylate (poly(C)), acting as the template at 6°C, 23°C and 37°C. In the absence of the template the major reaction pathway of 2-MeImpG is hydrolysis of the P-N bond to form the unreactive guanosine 5'-monophosphate (5'-GMP) and 2-methylimidazole. Concentrated solution of 2-MeImpG (>0.02 M) in the absence of the template form only small amount of dinucleotide, $(pG)_2$, but in the presence of poly(C), oligoguanylates, $(pG)_n$ with $2 \leq n \leq 40$, can be detected (Inoue and Orgel, 1982).

We were able to determine the rate constants for individual steps of this reaction. Our conclusions can be summarized as follows: (i) The effect of the template on the rate of the internucleotide bond formation, which corresponds to an approximately 200-fold catalysis (obtained from k_n/k_2 where k_n the biomolecular rate constant of reaction of an oligomer with $n \geq 5$ and k_2 the rate constant of dimerization of 2-MeImpG in the absence of poly(C) stays constant in the temperature range of 6°C to 37°C. This implies similar activation energies for the two reactions, i.e. the dimerization in the absence of the template and the elongation in the presence of the template. This result may suggest that the template acts as a site for bringing the reactants together without affecting the transition state of the internucleotide bond formation (not a true catalyst). (ii) In the early stages of the reaction hydrolysis of 2-MeImpG, initiation of the oligomerization (k_2, k_3 and k_4) and elongation (k_n, $5 \leq n \leq 11$), occur simultaneously and compete in such a way to give rise to a larger total percentage of shorter oligomers ($n<5$) at the lower temperature. This competition implies that for a constant supply of activated monomer the oligomerization process would favor longer oligomers at the higher temperature.

MACROMOLECULAR RECOGNITION: STRUCTURAL ASPECTS OF THE ORIGIN OF THE GENETIC SYSTEM

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Theoretical simulation of prebiotic chemical processes is an invaluable tool for probing the phenomenon of evolution of life. Using computational and modeling techniques and guided by analogies from present day systems we week to understand the emergence of the genetic apparatus, enzymatic catalysis and protein synthesis under prebiotic conditions.

Modeling of the ancestral aminoacyl-tRNA-synthetases (aRS) may provide important clues to the emergence of the genetic code and the protein synthetic machinery. Assuming that the catalytic function evolved before the elements of specific recognition for a particular amino acid, we are exploring the minimal structural requirements for the catalysis of tRNA aminoacylation. The first step reaction, a formation of an aminoacyl adenylate was studied in the framework of ab initio MO theory. Based on the available inhibitor-TyrRS complex, the role of individual residues in the vicinity of the TyrRS active site was examined. The effect of all possible amino acids substitutions near the active site was studied by estimating differential stabilization of the corresponding transition complex. Results indicated prominent catalytic role of His45, His48, Lys225, Lys230 and Lys233. Subsequent sequence analysis indicated that the pattern of these positively charged residues is conserved among different aRSs. This led us to propose a hypothesis that the three dimensional orientation of these positively charged residues may confer the essential catalytic role of the ancestral aRS. The second reaction, a formation of aminoacyl tRNA was studied by the molecular modeling system SYBYL with the high resolution crystallographic structures of the present day tRNA, aRSs complexes. The trinucleotide CCA of the 3'-end of tRNA is placed into the active site pocket of TyrRS, based upon the interaction scheme between tRNA^{Gln} and GlnRS, and upon the assumed stereochemistry of the TyrRS:tRNA:Tyr-AMP transition state.

In another possible scenario, RNA enzymatic reactions play a key role in the emergence of the self-replicating system offering a clue to the onset of enzymatic catalysis prior to the existence of the protein biosynthetic machinery. Our ultimate goal is to propose a simple RNA segment that is small enough to be built in the primordial chemical environment but maintains the specificity and catalytic activity of the contemporary RNA enzyme. To understand the mechanism of ribozyme catalyzed reactions, ab initio and semi-empirical (ZINDO) programs were used to investigate the reaction path of transphosphorylation. A special emphasis was placed on the possible catalytic and structural roles played by the coordinated magnesium cation. Both the inline and adjacent mechanisms of transphosphorylation have been studied. The structural characteristics of the target helices, particularly a possible role for the G•T pair, is also studied by molecular dynamics (MD) simulation technique.

THE 2.5-5.0 μM SPECTRA OF IO: EVIDENCE FOR H_2S AND H_2O FROZEN IN SO_2

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The techniques of low temperature spectroscopy are applied here to identify the constituents of the ices covering the surface of Io, a satellite of Jupiter.

Infrared spectra of Io in the 4000-2000 cm^{-1} region, including new observational data, are analyzed using laboratory studies of plausible surface ices.

Besides the well-known absorption bands attributable to sulfur dioxide frosts, four unidentified infrared spectral features of Io are pointed out. Two are at 2597 cm^{-1} and 2558 cm^{-1} and the second pair fall at 3367 cm^{-1} and 3175 cm^{-1}. These absorptions fall close to the fundamental X-H stretching modes in H_2S and H_2O respectively. The infrared absorption spectra of mixed molecular ices ranging from pure materials, to binary mixtures of H_2S and SO_2 (either mixed at different concentrations or layered), to $H_2O/H_2S/SO_2$ mixtures are discussed. The effects of ultraviolet irradiation (120 and 160 nm) and temperature variation (from 9 K to 130 K) on the infrared spectra of the ices are also examined. The comparative study shows that: (1) Io most likely contains H_2S and H_2O mixed with SO_2. The 2597 cm^{-1} and 2558 cm^{-1} bands in the Io spectra can be accounted for by the absorption of the S-H stretching vibration (ν_1) in H_2S aggregates and isolated molecules in an SO_2 matrix. The weak 3367 cm^{-1} and 3175 cm^{-1} bands which vary spatially and temporally in the Io spectra coincide with the ν_3 and ν_1 O-H stretching vibrations of clusters of H_2O complexed with SO_2. (2) The observations are well matched by SO_2.matrices containing about 3% H_2S and 0.1% H_2O and which have been formed by the condensation of a mixture of the gases onto a 100 K surface. (3) In the comparison of the spectra using the mixed molecular ice samples versus the layered ice samples only the former can explain the shifts and splitting of the absorption bands in the Io spectrum and account for the fact that solid H_2S is observed in the surface material of Io at temperatures and pressures above the sublimation point of pure H_2S. In addition to pointing out the presence of H_2S and H_2O on Io, the originality of this study comes from the fact that it is the first to consider mixed solids in carrying out laboratory simulations of planetary surfaces providing a realistic simulation of the "dirty" ices covering the surfaces of many satellites.

LABORATORY SIMULATION OF THE PHOTOPROCESSING AND WARM-UP OF COMETARY AND PRE-COMETARY ICES: PRODUCTION OF COMPLEX ORGANIC MOLECULES

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The recent missions to Comet Halley detected large quantities of organic material on grains as well as organic molecules in the gas phase. A possible origin of these materials is the energetic processing of ice mantles on the grains prior to comet formation, either in the pre-solar nebula or the interstellar medium. We simulated this process in the laboratory by depositing interstellar ice analogs ($H_2O/CH_3OH/CO/NH_3$) on a cold (10 K) substrate with simultaneous UV irradiation. The material evaporating during warm-up of the photolyzed ice as well as the residue remaining at room temperatures was analysed by a number of techniques. It was found that a large number of organic molecules of various complexity are synthesized during the simulation process, stressing the possible significance of UV photolysis for producing the organic Comet material.

BIOLOGICALLY CONTROLLED MINERALS AS POTENTIAL INDICATORS OF LIFE

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Minerals can be produced and deposited either by abiotic or biologic means. Regardless of their origin, mineral crystals reflect the environmental conditions (e.g., temperature, pressure, chemical composition, and redox potential) present during crystal formation. Biologically-produced mineral crystals are grown or reworked under the control of their host organism and reflect an environment different from the abiotic environment. For example, we have gathered sufficient evidence demonstrating that most biologically controlled minerals have attributes, such as morphologies and isotopic ratios, which differ from an abiotically produced mineral of the same chemical composition. In addition, minerals of either biologic or abiotic origin have great longevities. For these reasons, biologically produced minerals have been proposed as biomarkers. Biomarkers are key morphological, chemical, and isotopic signatures of living systems that can be used to determine if life processes have occurred.

To date, more than 60 different minerals have been identified as being produced or reworked by an assortment of organisms. Several of these minerals and the organisms that produce them have been well studied, such as magnetite produced by bacteria and aragonite produced by mollusks. Although some of the minerals produced by organisms, such as silica produced by diatoms, are abundant, very widely distributed, and have played an important role in the geologic record, much work still remains to be done.

The technique of using biologically-produced minerals as biomarkers has great potential and must be tested. The key to the use of minerals as biomarkers is the ability to distinguish between abiotically and biologically produced minerals. To accomplish this, universal traits unique to biologically controlled minerals must be identified. We have begun studies of biologically controlled minerals produced by the protist Paramecium tetraurelia since techniques have already been developed to culture them and isolate their crystalline material, and methods are already in place to analyze this material. Two direct crystalline phases have been identified. One phase, whose chemical composition is high in Mg, was identified as struvite. The second phase, whose chemical composition is high in Ca, has not been previously found occurring naturally and may be considered a newly discovered material. Analyses are currently underway to determine the characteristics of these minerals in order to compare them with characteristics of minerals formed abiotically, but with the same chemical composition.

PHOTOSYNTHETIC REACTION CENTER COMPLEXES FROM HELIOBACTERIA

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Photosynthetic reaction centers are pigment-protein complexes that are responsible for the transduction of light energy into chemical energy. Considerable evidence indicates that photosynthetic organisms were present very early in the evolution of life on Earth. The goal of this project is to understand the early evolutionary development of photosynthesis by examining the properties of reaction centers isolated from certain contemporary organisms that appear to contain the simplest photosynthetic reaction centers. The major focus of this project is the family of newly discovered strictly anaerobic photosynthetic organisms known as Heliobacteria. These organisms are the only known photosynthetic organisms that are grouped with the gram-positive phylum of bacteria. The properties of these reaction centers suggest that they may be the descendants of an ancestor that also gave rise to Photosystem I found in oxygen-evolving photosynthetic organisms.

Photoactive reaction center-core antenna complexes have been isolated from the photosynthetic bacteria *Heliobacillus mobilis* and *Heliobacterium gestii* by extraction of membranes with Deriphat 160C followed by differential centrifugation and sucrose density gradient centrifugation (Trost and Blankenship, Biochemistry 28, 9898-9904, 1989). The purified complexes contain one or more 48,000 Mr peptides that bind both the photoactive chlorophyll P800 and approximately 25 molecules of antenna bacteriochlorophyll *g*. Time-resolved fluorescence spectroscopy indicates that the antenna pigment are active in energy transfer to P800, exhibiting a major decay time of 25 ps in both membranes and reaction centers. The absorption and fluorescence properties of membranes and reaction centers are almost identical, suggesting that a single pigment-protein complex serves as both antenna and reaction center. Experiments in progress include sequence determination of the 48,000 Mr reaction center protein, and evolutionary comparisons with other reaction center proteins. These experiments are being done using chemical sequencing methods to obtain a partial sequence, followed by oligonucleotide synthesis and DNA hybridization to obtain the gene(s) for the protein(s).

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